INTERAGENCY COMPARISON BETWEEN ONTARIO AND MICHIGAN FOR CHLORIDE, NITROGEN AND PHOSPHORUS PARAMETERS

based on a special survey of range 3.9, stations 01-12, on the Detroit River

September 1975

Ministry of the Environment

The Honourable
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Minister

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NOTE:

Figures 1 - 6 of the report
are placed after the appendix.

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SEPTEMBER 1975

Based on a special survey of range 3.9,

stations 01 - 12 on the Detroit River.

Participants

Michigan Dept. of Natural Resources
Lansing, Michigan

Ontario Ministry of the Environment
Toronto, Ontario
London, Ontario

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ABSTRACT

Evaluation of chloride, nitrogen and phosphorus data obtained during a special survey of range 3.9 on the Detroit River, in which samples were split among three laboratories in Ontario and Michigan, shows that contamination of Ontario's sample containers occurred. The nature of the contaminant changed, during the day, from a phosphate species to a (metal) ammonium nitrate species of formula $M(NO_3)_2 \cdot NH_4NO_3$ and the source is suspected to be an airborne particulate. It is concluded that protection of containers against airborne particulate contaminants is critical to data quality.

The parameter list included ammonium, nitrate plus nitrite, total Kjeldahl nitrogen, total phosphorus, reactive phosphates and chloride. In spite of the level of contamination present in many of the samples, excellent agreement between Ontario and Michigan ammonium data was obtained after applying a correction to Ontario data equal to one-third of the difference in nitrate concentration reported by Ontario and Michigan. The chloride data was in good agreement between agencies, although there was some evidence of a bias. There was no sign of chloride contamination.

It is doubtful that the ammonium/nitrate relationship would have been as clear if Ontario's samples had not been field frozen over dry ice. Any move to discontinue field freezing should be considered in this light. Contamination of this magnitude has not been observed in past Ontario data, and normally would not be considered possible. However, because of a fluke of nature we have been able to identify a potential source of error which should be given serious consideration whenever future samples are taken.

INTRODUCTION

Six successive surveys were completed on September 23, 1975, of stations 01 - 12 range 3.9 on the Detroit River. Three runs (#1, 2, 3) were made by staff of the Michigan Department of Natural Resources (DNR), using their boat and routine sampling procedures, and three runs were made by staff of the Ontario Ministry of the Environment (MOE), using their boat and their routine sampling procedures. Samples were taken at 10 to 12 predetermined locations across the range and were split three ways for later analysis at each of the following laboratories:

Michigan DNR, Water Quality Control Lab, Lansing

Ontario MOE, Water Quality Section, Toronto

Ontario MOE, Regional Laboratory, London

The parameters measured were: chloride, ammonium, nitrate plus nitrite, total Kjeldahl nitrogen, total phosphorus and (filtered) reactive phosphates.

The original intent of the survey was to determine the accuracy of ship position location on the river, but it seemed useful to extend this to include an inter-laboratory comparison and data compatability study. This report examines the comparability of results reported by the three participating laboratories, and attempts to resolve the sources of observed discrepancies.

Containers and Preservation Techniques

Ontario: A portion of the sample collected was transferred into a prewashed, distilled water rinsed, 6 oz glass Prince of Wales bottle, and set aside for chloride analysis. No preservative was added and the container was not rinsed with sample. (For routine work, a 20 oz glass Boston Round bottle is used.

The portion for analysis of nitrogen and phosphorus parameters was transferred into a 200 ml wide mouth polystyrene container and frozen over dry ice. The container is used unwashed, as delivered from the manufacturer, and is not routinely rinsed with sample. Checks on these containers have shown no trace of contamination for N or P.

These containers and lids are received separately from the manufacturer in large sealed plastic bags. Lids are installed by staff of the Ontario Ministry of the Environment shipping section who pre-package the closed containers in sets of 24 for storage until needed.

These polystyrene containers can crack during freezing if overfilled with sample, but this is not routinely observed. (ie. overfilling is avoided).

Michigan: 125 ml linear polyethylene containers are used. They are flushed with sample during the sampling process. No preservative is added to the sample for chloride analysis. 5 drops of chloroform are added to the 125 ml sample for N and P analysis.

Sampling Techniques

Ontario: A 2 litre Kemmerer sampler was used to obtain a single sample of the river at each station. The water, so obtained, was then split among the three laboratories, into containers provided by the respective agencies.

Michigan: A special sampler, originally designed for DO sampling, was used. It holds four Michigan DNR sample containers in a special box. Four tubes run through four holes in the box and into the four sample containers. It is estimated that, in the process of sampling, the containers are flushed about three times while being filled with water. Two containers were removed and analysed by Michigan DNR. The contents of the other two containers were transferred to Ontario MOE containers, after which these two containers were placed back into the sampler. Ontario's portion was always taken from these same two Michigan containers.

DISCUSSION

The data is tabulated in the appendix which includes plots of concentration observed by each agency at each station for each run.

It is clear from these plots that data reported by Michigan DNR is consistent from run to run, independent of which agency was sampling. The small changes which occur from run to run appear to reflect a real change in river water quality since they are often accompanied by a similar change in one of the other parameters. This is particularly clear in the chloride data where the figures for each agency can be superimposed almost exactly (see figures 1a, 1b, 1c appendix).

However, when the results for nitrogen and phosphorus parameters are examined, it is apparent that gross contamination of the sample has occurred in Ontario samples relative to the data reported by Michigan DNR. The contaminants are ammonium, nitrate and phosphate at levels far in excess of what would be expected from a routine laboratory environment.

It is possible that the observed difference in data might not be contamination but rather a real difference in the samples received by the three laboratories. However, there was sufficient water from the Kemmerer sampler to split three ways. Since Michigan DNR results are consistent and low, the contamination occurred after the samples were split. (Obviously their containers were 'clean').

Since a large number of the containers used by Ontario MOE were received at the lab cracked, (probably due to over-filling of the containers prior to freezing) it is possible to speculate that the contamination occurred during transfer of the samples to the laboratories. However, many of the cracked containers showed no contamination, in spite of the extra manipulation of thawing the sample into a lab beaker and transferring it to a new container.

London laboratory's data is interesting in that the samples taken during runs 1 and 2 are grossly contaminated with phosphate, (see figure 4) but not at all with ammonium or nitrate. On the other hand their data from runs 3, 4, 5, and 6 shows gross ammonium and nitrate contamination but no phosphate contamination. A similar, although not exactly identical, pattern is present also in the Toronto laboratory data. (see figure 5). This suggests a time related source of contamination, occurring during the actual survey and not prior or subsequent to it.

Therefore, the source of contamination in Ontario MOE data was deduced to be associated with the sample containers and/or the way in which they were used. Figure 1 was plotted to determine whether the levels of nitrate and ammonium contamination were related. (An inverse relationship combined with bad scatter would point to the contaminant having been originally either nitrate or ammonium which had undergone biological or chemical conversion to produce the other. High levels of nitrite might be expected in such a case, but in fact, nitrite levels reported by Ontario were never greater than 0.015 mg N/l and were generally less than 0.008 mg N/l.)

The lack of scatter in figure 1 and the clear relationship of one ammonium as N per three nitrate as N, in spite of the range of concentration observed, points clearly to a contaminant with a well-defined chemical formulation such as

$$M(NO_3)_2 \cdot NH_4NO_3$$

where M is a divalent cation such as ferrous iron or two monovalent ions such as potassium. It could also be deduced that the clarity of the relationship was a direct result of the preservation-by-freezing technique used by Ontario MOE which prevented biological or chemical conversion. The standard deviation for estimating ammonium from nitrate contamination levels in figure 1 is 0.025 mg N/litre, which is comparable to Ontario MOE within-lab standard deviation at this level of concentration after allowance is made for the number of mathematical operations.

The level of contamination ranges from almost nil (less than 0.04 mg/l N) to as much as 1.4 mg/l of ammonia plus nitrate as N. If the metal were iron, this corresponds to between 0.15 and 5.2 mg of contaminant per 200 ml container, assuming only the pure salt and no other contaminant is present.

The range of contamination found suggests a particulate rather than a dissolved source for this salt. Its postulated structure is not suggestive of a laboratory based source. It is possible that the contaminant was airborne from some nearby chemical manufacturing complex or resulted from nearby

agricultural activities, and that it settled on (and into) the wide mouth polystyrene containers used by Ontario. (Winds at Windsor Airport were from the NNE at about 9 mph with gusts to 20 or 30 mph). Because containers and lids are not routinely rinsed with sample, this material dissolved in the sample and contaminated it.

Out of 96 containers used in runs 3 to 6, 38 were grossly contaminated with Nitrogen. (Only one sample from runs 1 and 2 shows the same pattern). Many of these were analysed at the Ontario London laboratory. It is striking that few of these samples showed serious orthophosphate contamination, although all 24 containers sent to London from runs 1 and 2 were contaminated with between 10 and 60 µg/l P. It is tempting to speculate that either a change in wind direction or a change in the manufacturing process, occurred between runs 2 and 3, and that this changed the particulate contamination from a phosphate to an ammonium nitrate species.

Interlaboratory Comparison

1. Ammonium - N

In order to demonstrate the precision and accuracy of Ontario MOE analytical procedures, figures 2 and 3 compare London MOE ammonium results to Michigan DNR data before and after correction for the presence of the contaminant. (See Table I). The corrected London result is obtained by calculating one-third of the difference between London and Michigan's nitrate plus nitrite results, and subtracting this from the ammonium level reported by London. Figure 3 clearly demonstrates the comparability of London and Michigan's ammonium data if the contaminant had not been present. There is no evidence of a significant difference in calibration between these labs. The observed scatter is comparable to the within-lab precision in spite of the number of mathematical operations involved. Since Toronto lab data is included in figure 1 it is apparent that a similar correction to Toronto data would be similarly effective. This was not done, however, because of the fewer number of contaminated samples received at Toronto.

2. Total Kjeldahl Nitrogen (TKN) as N

Both laboratories perform TKN analysis. Ontario reported TKN and ammonium-N results, whereas Michigan subtracted their TKN and ammonia data to obtain 'Organic-N', which they reported along with their ammonium-N result.

Obviously, the airborne contaminant affected Ontario's TKN results since TKN includes ammonium. However, if calculated Organic-N results are compared between Ontario and Michigan there is no evidence of significant bias. The between laboratory standard deviation is estimated as 0.06 mg/l N, which is comparable to the within-lab standard deviation of 0.03 - 0.05 mg/l N.

3. Nitrate plus Nitrite as N

The variation of nitrate present in the Detroit River at this range was not sufficient to permit interlab calibration.

The effectiveness of using the difference between Ontario and Michigan results to calculate an ammonium correction attests to the probable precision and absence of bias between laboratories.

4. Reactive Phosphates as P

There are several problems in interpreting the compatibility of Ontario and Michigan phosphate data.

a) Michigan preserves by means of chloroform.

b) Ontario preserves by freezing.

c) Michigan does not filter.

d) Ontario filters the thawed sample through glass fibre (Reeve Angel 934 AH).

e) There is strong evidence of contamination, particularly in runs 1 and 2, but carrying over into the later runs in Toronto's data as a more or less constant background particularly in runs 3, 4, and 5.

There is general agreement that reactive phosphates should be performed by on-site automated analytical procedures on samples filtered through 0.45 µm pore size filters such as Sartorius HA, specially packed without filter separators.

Since neither agency follows this procedure it is not clear how their data should be interpreted As expected, (see figures 4 and 5) there is evidence that Michigan's unfiltered data is higher than Ontario's filtered data if allowance is made for contamination in Ontario samples.

5. Total Phosphorus as P

Interpretation is difficult because of the extent of contamination present. If, however, the reactive phosphate result is subtracted from the total phosphorus value for each laboratory, there is general agreement between laboratories suggesting similar, if not identical, calibration slope. Between-lab standard deviation of about 0.006 mg P/l (see appendix) is not as good as expected, but considering the data available this is not surprising.

6. Chloride as Cl

Figure 6 shows a plot of difference between Michigan and Toronto chloride data versus Toronto's result. The scatter of data is better than one would expect based on within laboratory standard deviation and routine data reporting practices. It is apparent that there is no difference in slope calibration but Michigan data is high by about 1.8 mg/l Cl throughout the range 8 to 40 mg/l. This deviation was also observed in their analysis of a set of chloride standards prepared by London and circulated at the time of this survey.

Chloride mg/l

Theory	0.0	15.0	20.0
London	< 0.5	15.0	20.0
Toronto	< 0.1	15.0	20.5
Michigan	0.2	17.3	22.2

It was also observed, although not so clearly, in a series of round-robin samples prepared in December, 1975, by Toronto for PLUARG analysts in which Michigan participated.

Samples	1	2	3	4	5
Toronto	13.5	17.0	3.5	30.0	38.5
London	13.5	16.5	3.5	30.5	38
Thunder Bay	13.9	16.3	2.9	30.1	39.2
Michigan	14.3	18.1	3.9	31.4	40.0

At the time of preparing this report, Mr. Peck, at the Michigan DNR laboratory, felt that the source of bias had been corrected, but for most purposes it is not a severe problem.

Conclusions

There is sufficient data to suggest no serious problems exist with respect to analytical calibration in terms of inter-lab comparison. However, phosphate analysis procedures are not comparable between Michigan and Ontario, although the resulting data may be useful to each agency. Chloride inter-comparison was excellent except for a slight bias.

Whether or not the samples became contaminated with phosphate and ammonium nitrate in the way postulated, it is apparent that sample containers and lids must be rinsed with sample. Lids should be kept on the containers at all times.

It is doubtful that the ammonium/nitrate relationship would have been as clear if Ontario's samples had not been field frozen over dry ice. Any move to discontinue field freezing should be considered in this light.

A similar study, including other routine parameters, would be useful. Steps should be initiated to re-do this survey at an earlier date. If the survey is repeated, the nutrient parameters should be performed on both frozen and unfrozen samples. It would also be of value to spike some of the field samples with phosphate and ammonium to observe the effect of sample handling and preservation on significant levels of the parameters of interest.

In closing, it should be noted that contamination of this magnitude has not been observed in past Ontario data, and normally would not be considered possible. However, because of a fluke of nature we have been able to identify a potential source of error which should be given serious consideration whenever future samples are taken.

ACKNOWLEDGEMENTS

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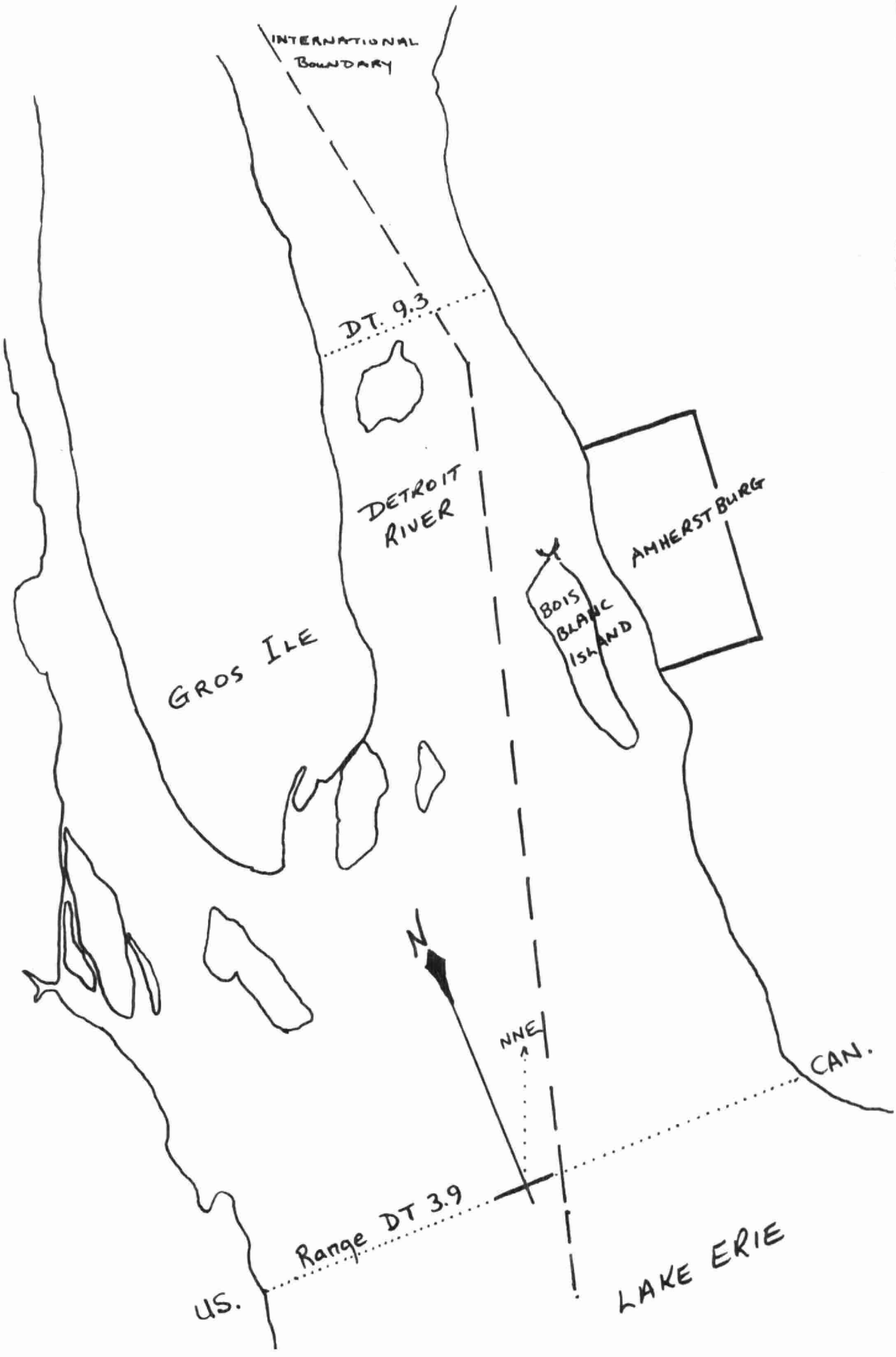
TABLE OF CORRECTIONS

for contaminant in London NH_4 data

Correction is 1/3 difference between London and Michigan's nitrate and nitrite data, using data from runs 3, 4, 5, 6.

	excess NO_3	London NH_4 orig.	London NH_4 corr.	Mich. NH_4
run 3	-	.38	-	-
	.46	.57	.416	.31
	.79	.51	.313	.24
	.20	.28	.213	.20
	.04	.105	.092	.088
	.03	.065	.055	.054
	.03	.055	.045	.042
	.03	.025	.015	.017
	.05	.035	.018	.012
	.13	.055	.012	.012
	.10	.070	.033	.020
	-	.215	-	-
run 4	(-.01)	.28	-	.35
	.07	.345	.322	.31
	.09	.270	.240	.22
	.04	.170	.157	.154
	.11	.075	.048	.053
	.29	.150	.053	.050
	.06	.040	.020	.028
	.05	.030	.013	.016
	.64	.250	.037	.009
	.56	.155	(-.032)	.009
	.25	.125	.042	.035
	.46	.265	.112	.054
run 5	.21	.45	.38	.36
	.04	.35	.337	.33
	.55	.445	.262	.24
	.23	.185	.108	.096
	.09	.080	.050	.048
	1.05	.440	.090	.046
	.08	.040	.013	.012
	.30	.125	.025	.010
	.08	.060	.033	.010
	.29	.100	.003	.011
	.00	(.47)	-	.024
	.11	.100	.063	.065
run 6	.05	.370	.353	.34
	.08	.370	.343	.34
	.02	.235	.228	.24
	.06	.125	.105	.121
	.05	.065	.048	.051
	.12	.115	.075	.043
	.40	.130	-.003	.021
	.04	.025	.012	.011
	.06	.035	.015	.008
	.14	.070	.033	.009
	.08	.050	.033	.023
	.04	.075	.062	.062


INTERNATIONAL BOUNDARY
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DETROIT RIVER
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Range DT 3.9
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LAKE ERIE

APPENDIX TO DETROIT R. SURVEY REPORT

The following tables of data were compiled for results reported by three laboratories on six parameters. Samples were taken at stations 01 to 12 at range DT 3.9 on the Detroit River on six successive runs on 23 September, 1975.

Runs 1, 2, 3 Michigan sampled

Runs 4, 5, 6 Ontario sampled

Stations number from US side, all runs started at station 01.

Laboratories M: Michigan, DNR, Lansing
T: Ontario MOE, Toronto
L: Ontario MOE, London

Circled data: suspiciously gross difference

Small circle in left corner: container cracked on arrival at lab.

Figures a) concentration vs station number, Michigan
b) " " " " London
c) " " " " Toronto
d) regression analysis: - L vs T
- L vs M
- T vs M
excluding circled data

equations: $Y = (\text{slope})_{y.x} X + (\text{intercept}) \pm s_{y.x.}$

$Y = (\text{slope})_{x.y.} X + (\text{intercept}) \pm s_{x.y}$

$s_{y.x.}$ = standard deviation of estimating Y given X

$s_{x.y.}$ = standard deviation of estimating X given Y

Tables 1. Chloride as Cl
2. Ammonium as N
3. Nitrate + Nitrite as N
4. Total Kjeldahl Nitrogen as N
5. (TKN - NH_4) = 'Organic N' as N
6. Reactive Phosphates: (Mich. unfiltered) as P
(Ont. filtered) as P
7. Total Phosphorus as P
8. Total P - Reactive PO_4 as P

TABLE I

CHLORIDE mg/l

	Run 1			Run 2			Run 3			Run 4			Run 5			Run 6		
	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L
1.	/	18.5	18.0	/	19	18.5	/	18.5	18.5	21	19.5	19.0	22	20	19.5	19	16.5	16.0
2.	15	13.5	13.0	18	15.5	15.5	18	16.5	16.0	16	14.5	14.0	18	16	15.5	17	14.5	14.0
3.	13	10.5	10.0	12	10.5	10.0	13	11	10.0	13	11	10.5	13	11	10.0	12	10.5	9.7
4.	11	9.3	8.8	16	14	13.5	13	11	10.5	16	14.5	14.5	11	8.8	8.6	14	12	11.5
5.	10	8.2	7.9	10	8.4	8.0	12	11	10.0	9.5	7.6	7.4	9.4	7.5	7.4	9.3	7.4	7.4
6.	9.3	8.2	7.3	9.3	7.8	7.3	9.4	7.8	7.4	9.3	7.6	7.3	9.4	7.4	7.3	9.3	7.2	7.4
7.	9.8	7.6	7.8	9.5	8.2	7.5	9.3	7.5	7.8	11	8.7	8.4	13	11	10.0	10	8.0	8.0
8.	10	8.1	8.0	10	8.5	8.2	11	8.7	8.4	12	11	10.0	13	11	10.0	12	10.5 ~~9.6~~	9.8
9.	18	15.5	15.5	23	21	20.0	15	13	12.5	24	22	21.0	24	22.5	21.5	23	21.5	20.5
10.	26	24	23.5	24	23	22.5	24	22.5	22.0	26	24	23.0	26	24	23.0	26	23.5	23.0
11.	22	20	19.5	22	20	20.0	21	19.5	19.5	34	32	30.5	27	25	24.0	22	20.5	19.5
12.	/	32	31.0	/	32	31.5	/	32.	31.0	43	42	39.0	42	40	38.5	40	40	38.0

TABLE 2

AMMONIA mg N/l

	Run 1			Run 2			Run 3			Run 4			Run 5			Run 6		
	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L
1.	/	.365	.360	/	.425	.370	/	.375	.380	.35	.40	.280	.36	.395	.450	.34	.40	.370
2.	.27	.290	.290	.30	.325	.320	.31	.340	.570	.31	.330	.345	.33	.360	.350	.34	.340	.370
3.	.21	.210	.200	.22	.235	.210	.24	.250	.510	.22	.240	.270	.24	.240	.445	.24	.430	.235
4.	.069	.070	.175	.182	.170	.180	.20	.205	.280	.154	.165	.170	.096	.090	.185	.121	.325	.125
5.	.066	.070	.075	.087	.20	.090	.088	.090	.105	.053	.050	.075	.048	.050	.080	.051	.060	.065
6.	.035	.035	.040	.049	.325	.050	.054	.055	.065	.050	.050	.150	.046	.045	.440	.043	.085	.115
7.	.026	.030	.030	.033	.035	.050	.042	.050	.055	.028	.210	.040	.012	.015	.040	.021	.015	.130
8.	.022	.030	.030	.018	.020	.025	.017	.020	.025	.016	.020	.030	.010	.015	.125	.011	.140	.025
9.	.010	.015	.035	.011	.005	.020	.012	.015	.035	.009	.150	.250	.010	.010	.060	.008	.010	.035
10.	.009	.015	.015	.010	.010	.020	.012	.015	.055	.009	.130	.155	.011	.015	.100	.009	.010	.070
11.	.017	.020	.025	.017	.015	.020	.020	.020	.070	.035	.20	.125	.024	.030	.470	.023	.230	.050
12.	/	.040	.040	/	.035	.045	/	.040	.215	.054	.245	.265	.065	.070	.100	.062	.070	.075

TABLE 3

NITRATE + NITRITE mg N/l

	Run 1			Run 2			Run 3			Run 4			Run 5			Run 6		
	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L
1.	/	°.24	.26	/	.225	.25	/	.23	(.16)	.24	°.245	°.23	.23	.24	(.44)	.23	(.65)	°.28
2.	.22	.23	.24	.22	(.71)	.24	.23	.24	(.69)	.23	.235	.30	.22	°.225	.26	.22	.235	.30
3.	.22	.225	.24	.22	.24	°.25	.22	.225	(1.01)	.22	°.225	°.31	.21	.225	(.76)	.22	(.735)	°.24
4.	.23	.24	.25	.22	.25	.24	.23	.235	(.43)	.23	°.245	°.27	.22	°.21	(.45)	.24	(.87)	°.30
5.	.22	.225	.24	.22	(.545)	.24	.23	.245	.27	.22	°.21	(.33)	.21	°.20	(.30)	.21	.24	°.26
6.	.21	°.22	°.27	.21	°.20	°.24	.21	.225	°.24	.21	°.215	(.50)	.22	°.20	(1.27)	.21	(.345)	(.33)
7.	.21	.225	.25	.22	.23	.27	.21	.23	°.24	.22	(.845)	°.28	.21	°.215	(.29)	.22	°.21	(.62)
8.	.21	.22	°.23	.21	.235	.23	.22	.23	.25	.22	.23	°.27	.22	°.21	(.52)	.21	°.65	°.25
9.	.22	.24	.26	.23	.25	.26	.22	.24	°.27	.24	(.59)	(.88)	.24	°.24	(.32)	.23	°.245	°.29
10.	.25	.26	.28	.24	.255	.27	.24	.255	(.37)	.24	(.53)	(.80)	.25	°.255	(.54)	.23	°.245	(.37)
11.	.30	.34	.32	.30	.315	.37	.30	.315	°.40	.31	(.805)	(.56)	.30	°.30	°.30	.28	(.815)	°.36
12.	/	.34	.34	/	.35	.32	/	.34	(.75)	.33	(.84)	°.79	.33	.33	(.44)	.32	°.325	.36

TABLE 4

TOTAL KJELDAHL N

mg N/l

	Run 1			Run 2			Run 3			Run 4			Run 5			Run 6		
	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L
1.	/	.765	.770	/	(1.35)	.800	/	.618	.735	.90?	.910?	.700?	.87	.810	.890	.76	.930	.810
2.	.66	.629	.645	.68	.789	.670	.72	.615	(.930)	.83	.760	.760	.74	.720	.695	.71	.635	.750
3.	.50	.460	.515	.55	.470	.615	.59	.462	(.925)	.60	.490	(.780)	.60	.479	(.845)	.51	(.770)	.520
4.	.319	.300	.330	.502	.428	.490	.50	.460	.665	.474	.395	.515	.426	.269	(.640)	.351	(.640)	.450
5.	.316	(.492)	.350	.317	.390	.370	.348	.298	.355	.293	.230	.365	.288	.229	(.400)	.191	.280	.300
6.	.235	.268	.265	.239	(.70)	.260	.254	.228	.310	.350	.245	(.485)	.256	.250	(.830)	.223	.272	.305
7.	.186	.218	.210	.203	.20	.270	.242	.220	.265	.318	(.50)	.295	.152	.200	(.350)	.161	.180	(.320)
8.	.182	.221	.255	.218	.215	.240	.227	.231	.285	.266	.220	.230	.150	.180	(.465)	.121	(.430)	.265
9.	.180	.228	(.410)	.181	.219	.270	.182	.177	.300	.319	.391	(.620)	.210	.218	(.470)	.118	.220	.300
10.	.149	.191	.250	.200	.210	.220	.202	.198	.290	.259	.390	.400	.181	.225	(.510)	.139	.210	(.520)
11.	.217	.319	.280	.267	.242	.230	.270	.250	(.450)	.305	.570	.450	.254	.296	(.885)	.223	(.512)	.405
12.	/	.225	.335	/	.309	.500	/	.320	.570	.384	.641	(.830)	.315	.325	(.590)	.332	(.540)	.370

TABLE 5

TOTAL KJELDAHL N MINUS AMMONIA mg N/l

	Run 1			Run 2			Run 3			Run 4			Run 5			Run 6		
	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L
1.	/	.40	.43	/	.92	.43	/	.34	.35	.55	.51	(.42)	.51	.41	.44	.42	(.53)	.44
2.	.39	.34	.36	.38	.46	.45	.41	.38	.36	(.52)	.43	.41	.41	.36	.35	.37	.30	.38
3.	.29	.25	.32	.33	(.23)	.40	.35	.21	.41	.38	.25	(.51)	.36	.24	.40	.27	.34	.28
4.	.25	.23	.15	.32	.26	.31	.30	.25	.38	.32	.23	.34	.33	.18	(.53)	.23	.31	.33
5.	.25	(.42)	.27	.23	.19	.29	.26	.21	.25	.24	.18	.29	.24	.18	(.32)	.14	.22	.23
6.	.20	.23	.23	.19	(.37)	.21	.20	.17	.25	.30	.20	.33	.21	.21	(.39)	.18	.20	.19
7.	.16	.19	.18	.17	.16	.22	.20	.17	.21	.29	.29	.26	.14	.18	(.31)	.14	.16	.19
8.	.16	.19	.22	.20	.20	.21	.21	.21	.26	.25	.20	.20	.14	.16	(.34)	.11	.29	.24
9.	.17	.21	(.37)	.17	.21	.25	.17	.16	.26	.31	.24	(.37)	.20	.21	(.41)	.11	.21	.27
10.	.14	.17	.24	.19	.20	.20	.19	.18	.24	.25	.26	.26	.17	.21	(.80)	.13	.20	(.45)
11.	.20	.30	.26	.25	.23	.21	.25	.23	(.38)	.27	.37	.32	.23	.27	(.41)	.20	.28	.36
12.	/	.18	.30	/	.27	(.45)	/	.28	(.45)	.33	.39	(.57)	.25	.25	(.49)	.27	(.47)	.30

TABLE 6

REACTIVE PHOSPHATES (ONTARIO FILTERED) mg P/l

	Run 1			Run 2			Run 3			Run 4			Run 5			Run 6		
	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L
1.	/	.10	.058	/	.051	.064	/	.087	.046	.076	.080	.020	.078	.079	.049	.064	.051	.038
2.	.047	.055	.050	.060	.051	.083	.059	.078	.049	.056	.062	.034	.060	.062	.037	.053	.046	.033
3.	.030	.050	.038	.032	.047	.033	.037	.045	.021	.031	.038	.018	.031	.042	.013	.030	.027	.015
4.	.013	.015	.026	.029	.024	.030	.030	.054	.027	.021	.034	.030	.014	.030	.012	.020	.019	.013
5.	.010	.054	.034	.015	.016	.077	.013	.030	.021	.009	.015	.016	.007	.015	.012	.009	.013	.010
6.	.007	.051	.066	.010	.012	.037	.010	.017	.012	.009	.040	.008	.008	.030	.011	.007	.012	.014
7.	.007	.023	.027	.008	.022	.019	.006	.023	.007	.003	.012	.008	.003	.015	.014	.006	.007	.009
8.	.005	~~.093~~ .092	.022	.005	.014	.028	.006	.027	.006	.005	.007	.007	.003	.013	.010	.003	.009	.006
9.	.004	.050	.025	.005	.019	.057	.006	.120	.008	.005	.008	.007	.004	.019	.011	.003	.005	.006
10.	.004	.012	.055	.005	.008	.166	.005	.023	.007	.005	.006	.007	.005	.016	.008	.003	.002	.009
11.	.005	.044	.019	.008	.013	.019	.005	.017	.007	.006	.011	.005	.004	.012	.009	.006	.005	.008
12.	/	.015	.020	/	.023	.064	/	.028	.009	.007	.009	.010	.007	.029	.008	.008	.009	.004

TABLE 7

TOTAL PHOSPHORUS

mg P/l

	Run 1			Run 2			Run 3			Run 4			Run 5			Run 6		
	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L
1.	/	.145	.140	/	.108	.153	/	.151	.130	.127	.117	.145	.145	.133	.137	.121	.063	.121
2.	.086	.138	.104	.099	.086	.152	.111	.126	.110	.091	.084	.101	.106	.094	.098	.091	.081	.096
3.	.060	.070	.084	.073	.062	.087	.073	.076	.084	.057	.070	.063	.065	.077	.064	.059	.054	.060
4.	.044	.025	.047	.058	.051	.073	.055	.081	.094	.043	.056	.074	.035	.037	.044	.041	.045	.040
5.	.038	.064	.065	.036	.031	.108	.034	.050	.036	.019	.032	.034	.023	.028	.028	.020	.026	.025
6.	.047	.067	.094	.027	.027	.052	.025	.029	.022	.021	.058	.027	.029	.045	.033	.020	.021	.036
7.	.015	.034	.050	.024	.031	.026	.027	.036	.018	.010	.022	.024	.014	.024	.026	.014	.014	.024
8.	.006	.022	.034	.025	.027	.042	.013	.049	.014	.013	.014	.017	.017	.021	.032	.011	.022	.016
9.	.007	.058	.058	.021	.029	.073	.012	.138	.016	.012	.020	.029	.017	.027	.019	.011	.026	.019
10.	.021	.019	.079	.020	.016	.188	.015	.034	.022	.010	.015	.023	.012	.027	.021	.011	.016	.022
11.	.019	.069	.042	.019	.026	.052	.021	.036	.027	.017	.029	.025	.018	.025	.046	.018	.021	.021
12.	/	.031	.037	/	.047	.084	/	.047	.034	.020	.030	.051	.024	.045	.027	.023	.077	.025

TABLE 8

TOTAL P – REACTIVE PO_4

mg P/litre

	Run 1			Run 2			Run 3			Run 4			Run 5			Run 6		
	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L	M	T	L
1.	/	.045	.082	/	.057	.089	/	.064	.084	.051	.037	.125	.067	.054	.088	.057	.012	.083
2.	.039	.083	.054	.039	.035	.069	.052	.048	.061	.035	.022	.067	.046	.032	.061	.038	.035	.063
3.	.030	.020	.046	.041	.015	.054	.036	.031	.063	.026	.032	.045	.034	.035	.051	.029	.027	.045
4.	.031	.010	.021	.029	.027	.043	.025	.027	.067	.022	.022	.044	.021	.007	.032	.021	.026	.027
5.	.028	.010	.031	.021	.015	.031	.021	.020	.015	.010	.017	.018	.016	.007	.016	.011	.013	.015
6.	.040	.016	.028	.017	.025	.015	.015	.012	.010	.012	.018	.019	.021	.015	.022	.013	.009	.022
7.	.008	.012	.023	.016	.009	.007	.021	.013	.011	.007	.010	.016	.011	.009	.012	.008	.007	.015
8.	.001	.020	.012	.020	.013	.014	.007	.022	.008	.008	.007	.010	.014	.009	.022	.008	.013	.010
9.	.003	.008	.033	.016	.010	.016	.006	.018	.008	.007	.012	.022	.013	.008	.008	.008	.021	.013
10.	.017	.007	.024	.015	.008	.022	.010	.011	.015	.005	.009	.016	.007	.011	.013	.008	.014	.013
11.	.014	.025	.023	.011	.013	.033	.016	.019	.020	.011	.018	.020	.014	.013	.037	.012	.016	.013
12.	/	.016	.017	/	.024	.020	/	.019	.025	.013	.021	.041	.017	.016	.019	.015	.068	.021

Figure 1a)

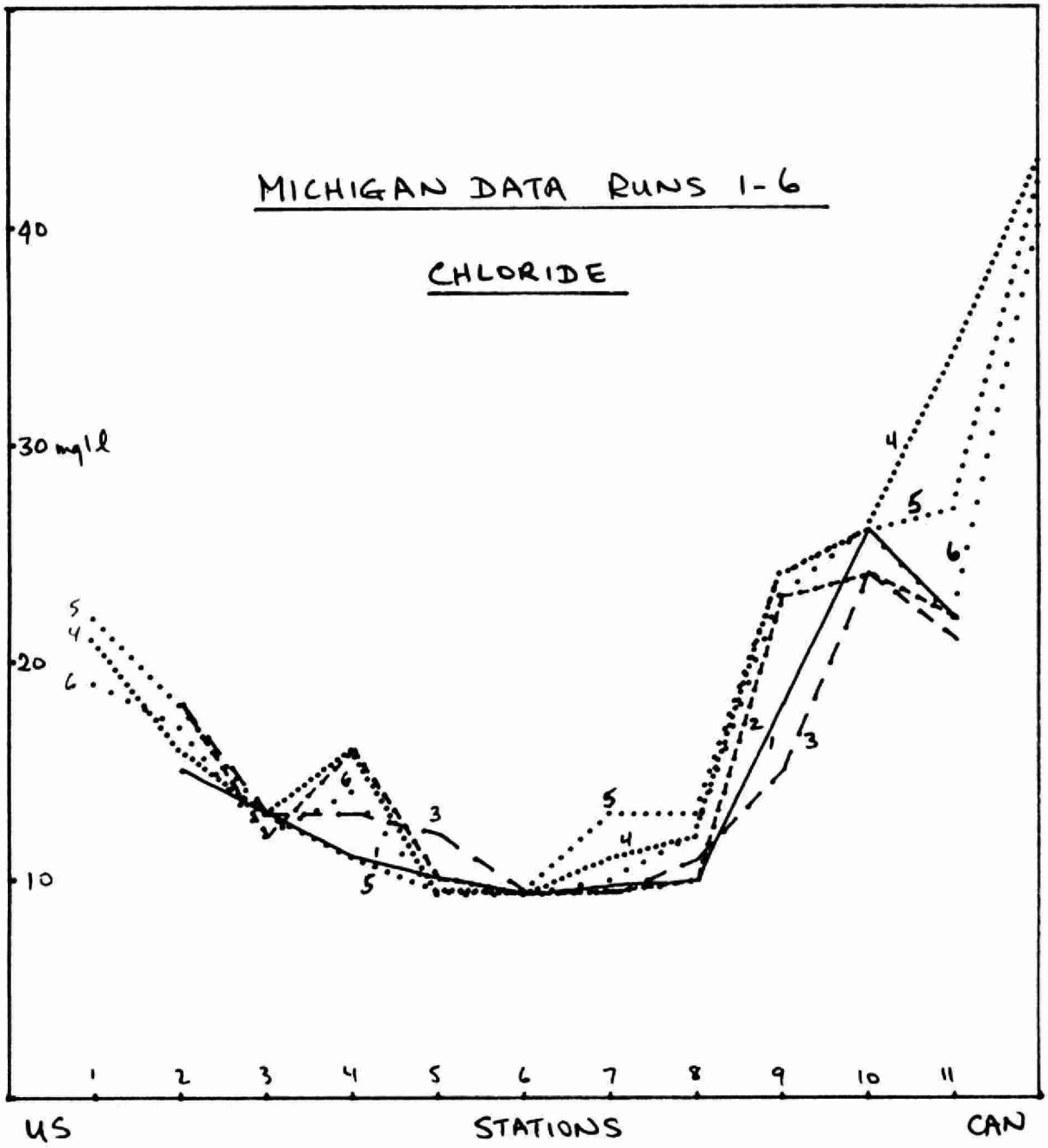

MICHIGAN DATA RUNS 1-6
CHLORIDE
40
30 mg/l
20
10
1
2
3
4
5
6
7
8
9
10
11
US
STATIONS
CAN

Figure 1b)

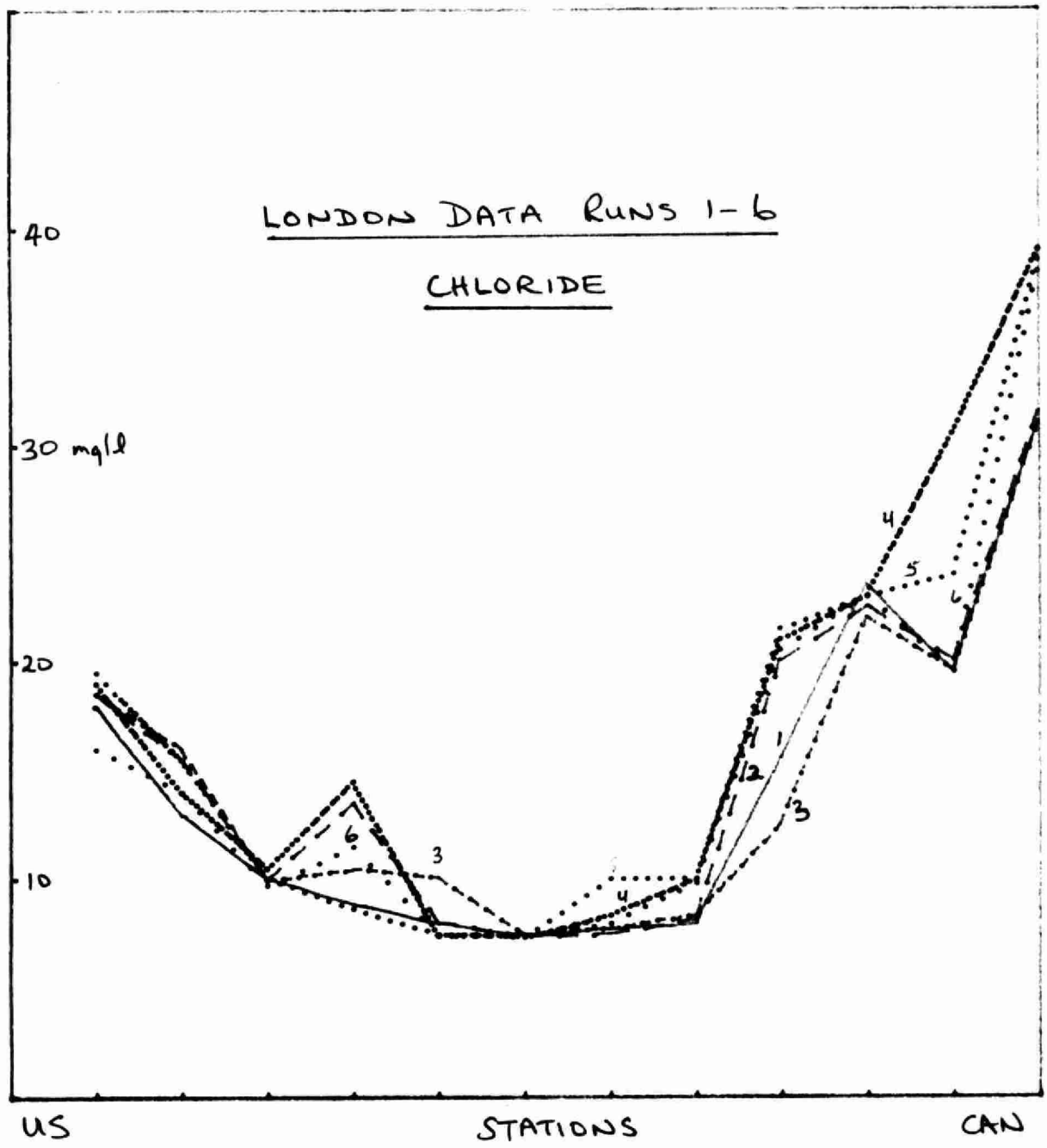


Figure 1c)

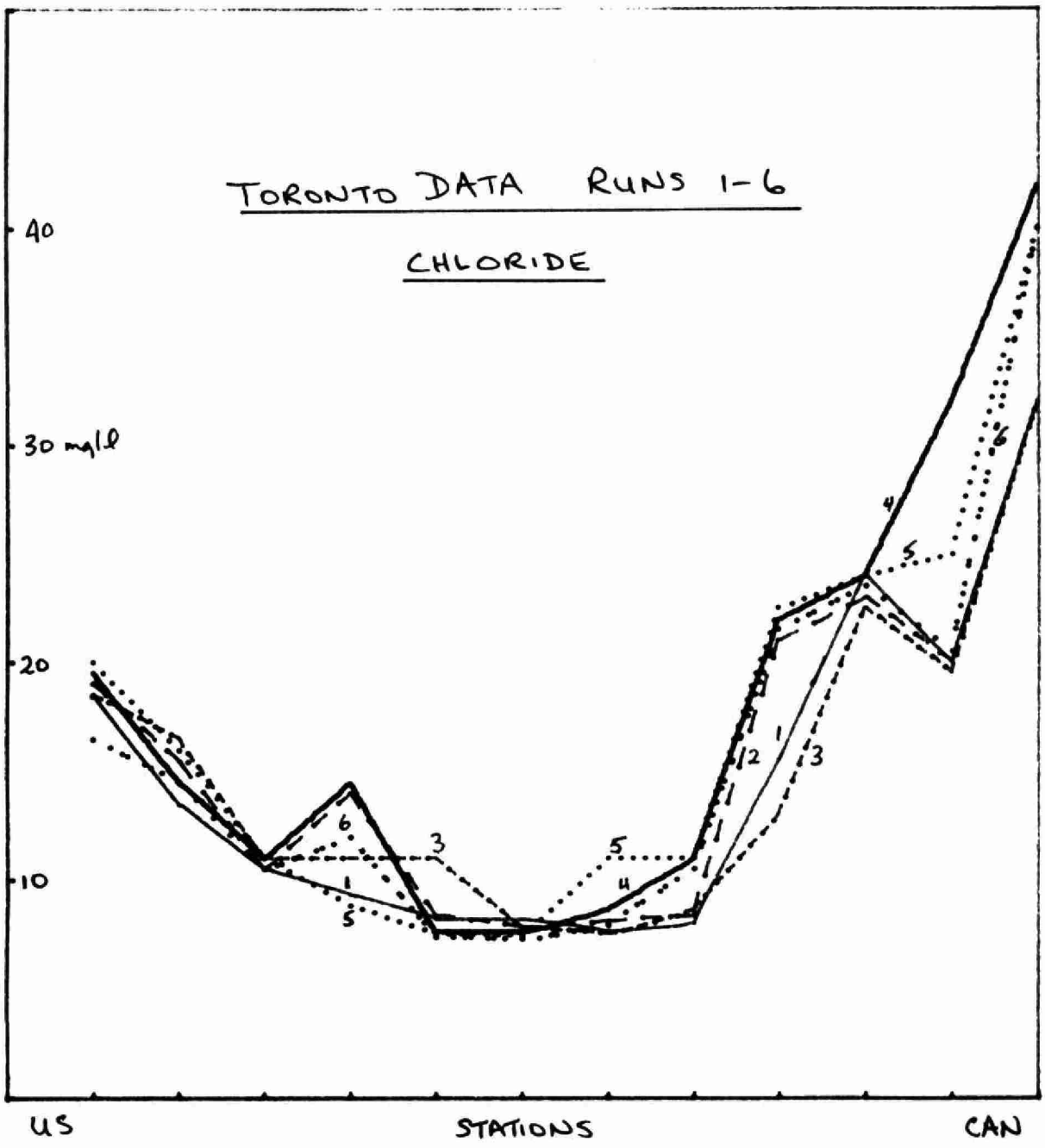


Figure 1 d)

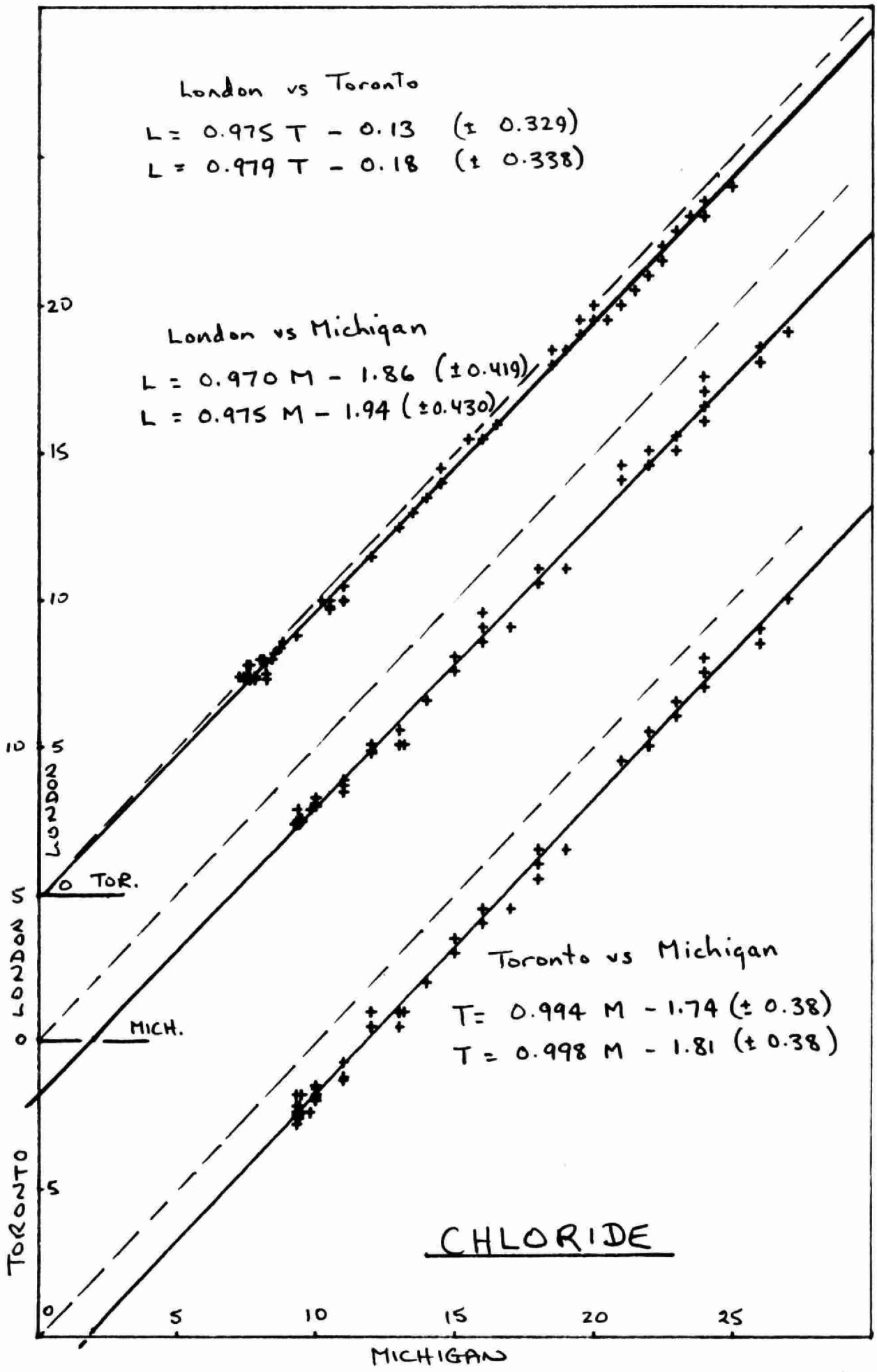
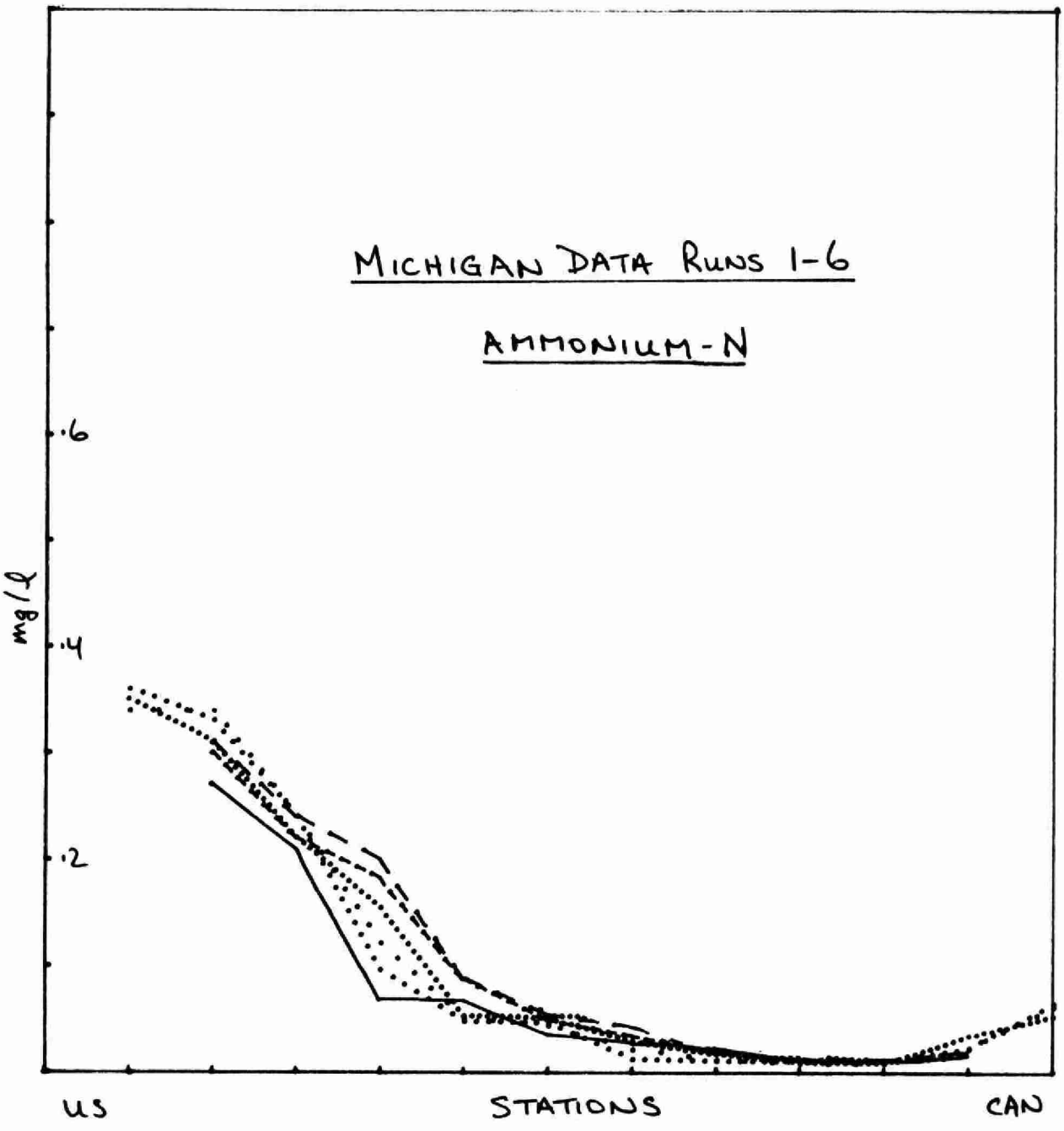
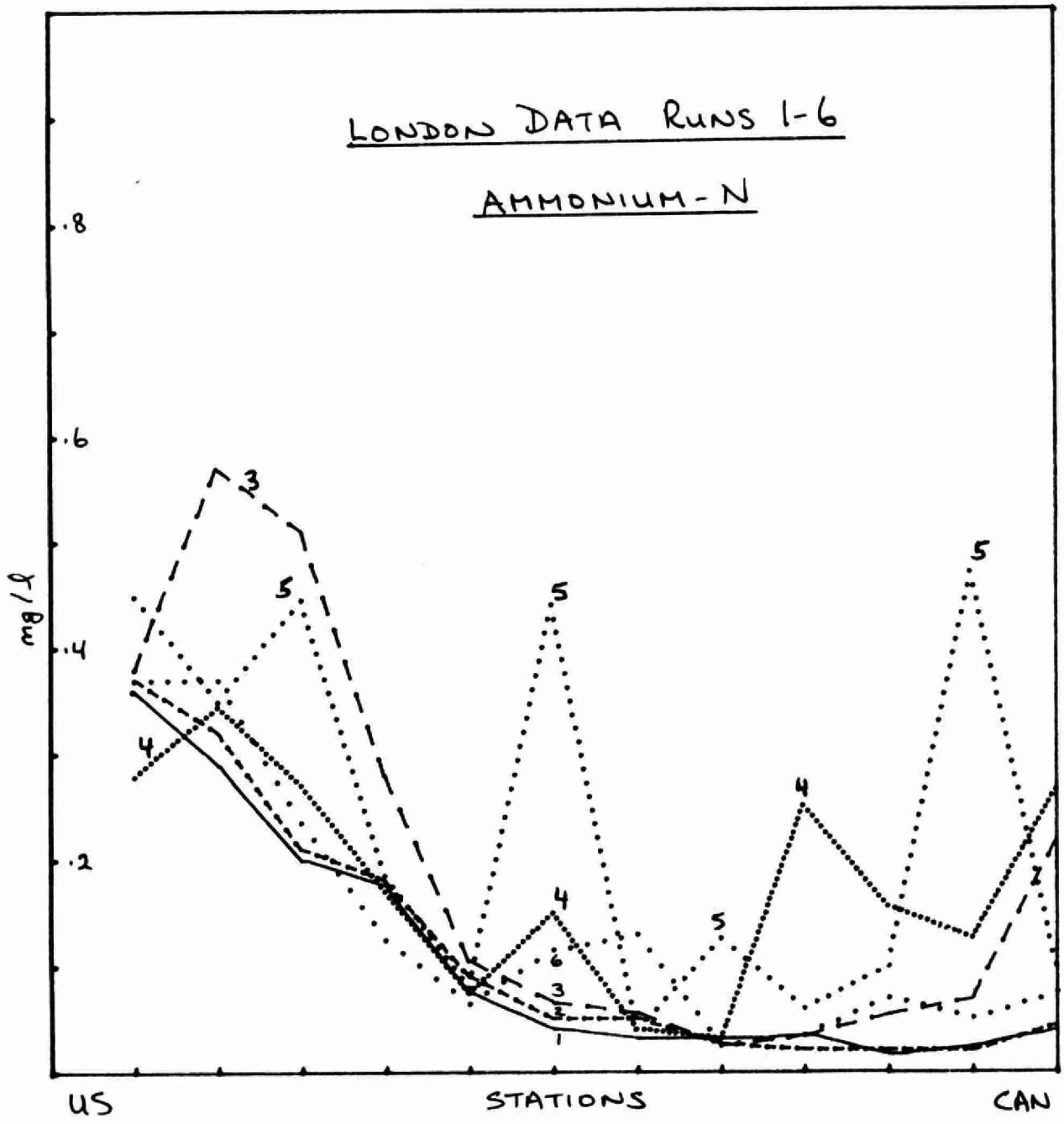

London vs Toronto
L = 0.975 T - 0.13 (± 0.329)
L = 0.979 T - 0.18 (± 0.338)
London vs Michigan
L = 0.970 M - 1.86 (±0.419)
L = 0.975 M - 1.94 (±0.430)
Toronto vs Michigan
T = 0.994 M - 1.74 (± 0.38)
T = 0.998 M - 1.81 (± 0.38)
CHLORIDE
LONDON
TORONTO
MICHIGAN
TOR.
MICH.
0
5
10
15
20
25

Figure 2a)



MICH NH3 1

Figure 2b)



LNH 1

Figure 2c)

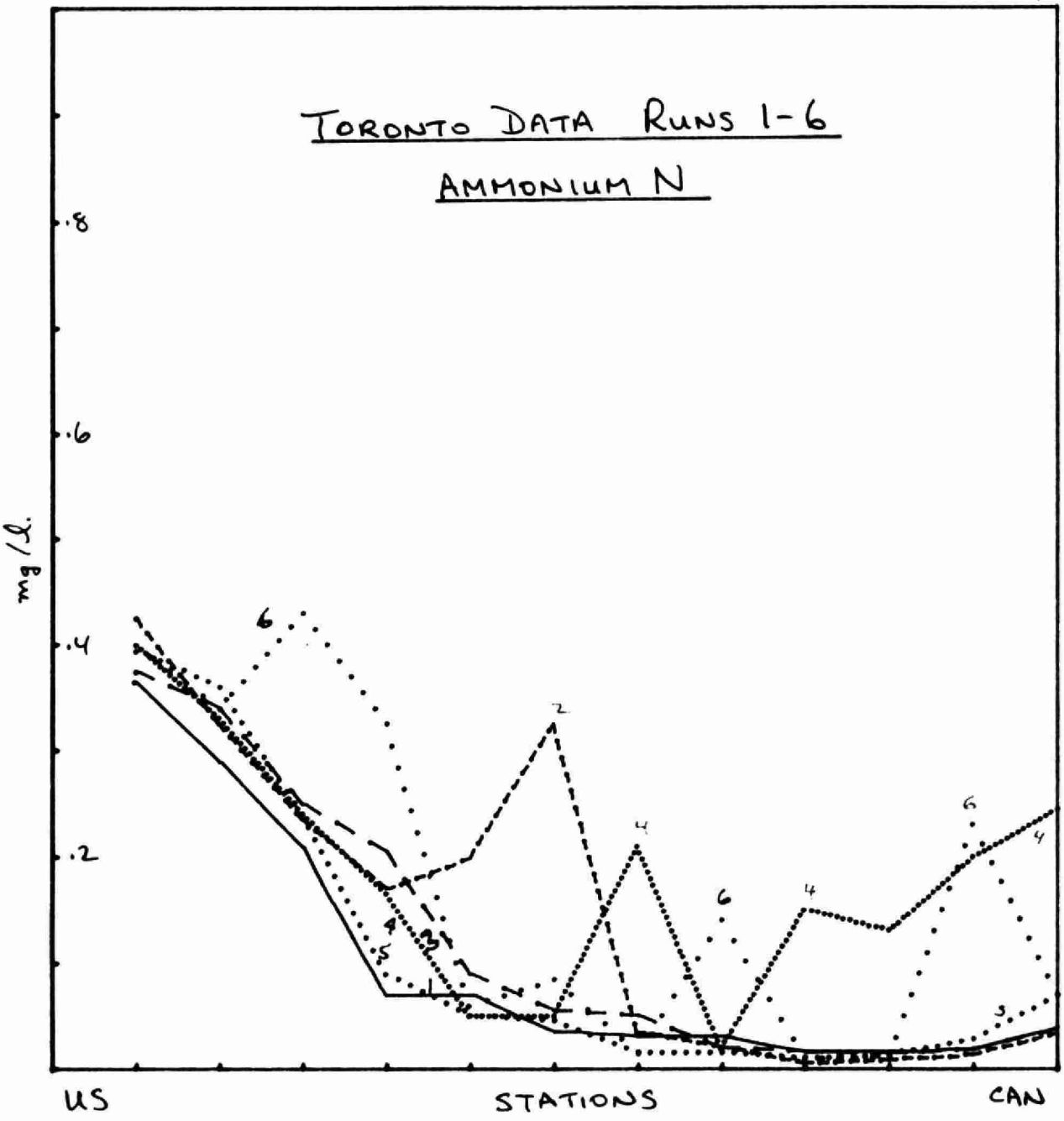


Figure 2 d)

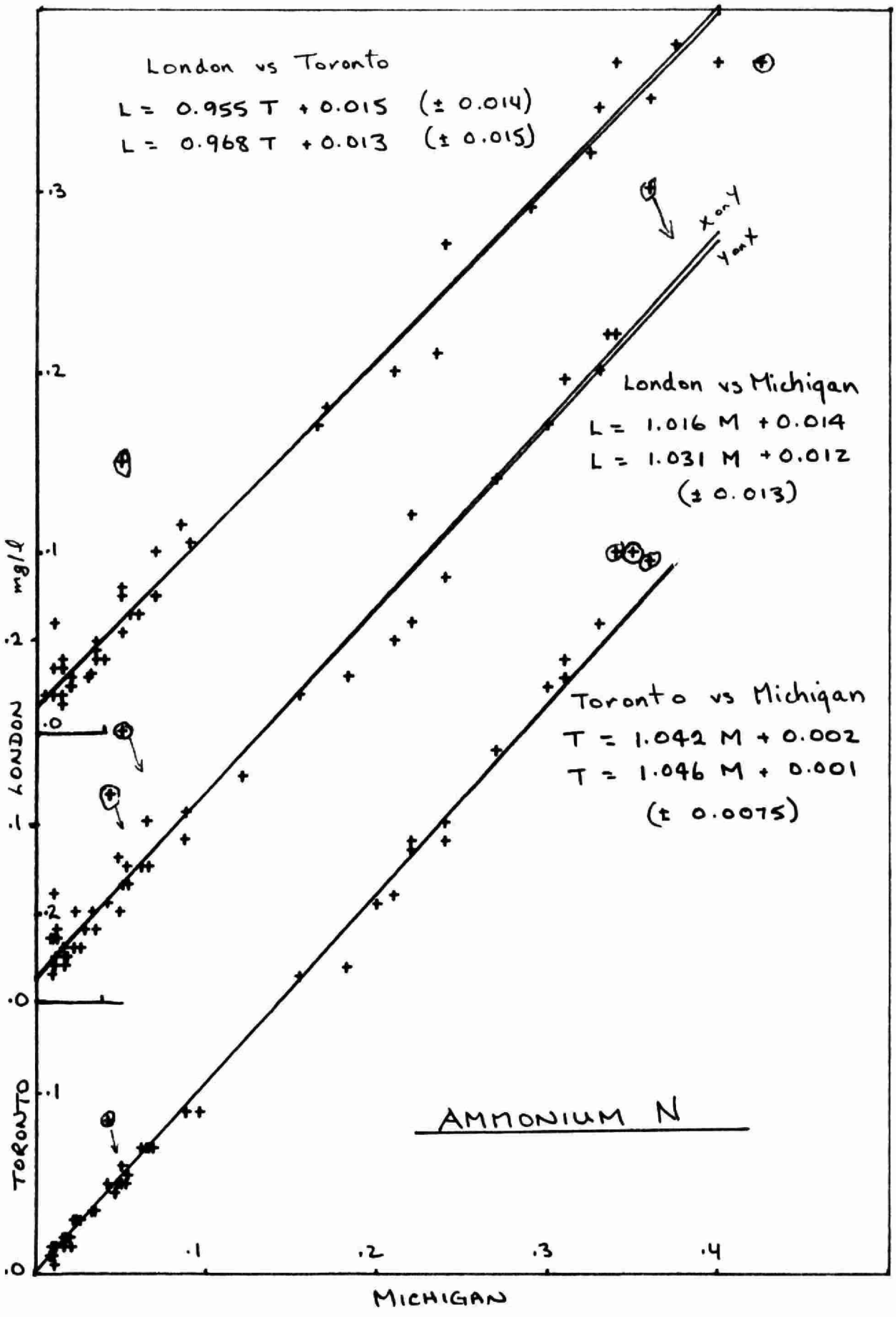

London vs Toronto
L = 0.955 T + 0.015 (± 0.014)
L = 0.968 T + 0.013 (± 0.015)
x only
y only
London vs Michigan
L = 1.016 M + 0.014
L = 1.031 M + 0.012
(± 0.013)
Toronto vs Michigan
T = 1.042 M + 0.002
T = 1.046 M + 0.001
(± 0.0075)
AMMONIUM N
LONDON mg/l
TORONTO
MICHIGAN
.0
.1
.2
.3
.4

Figure 3a)

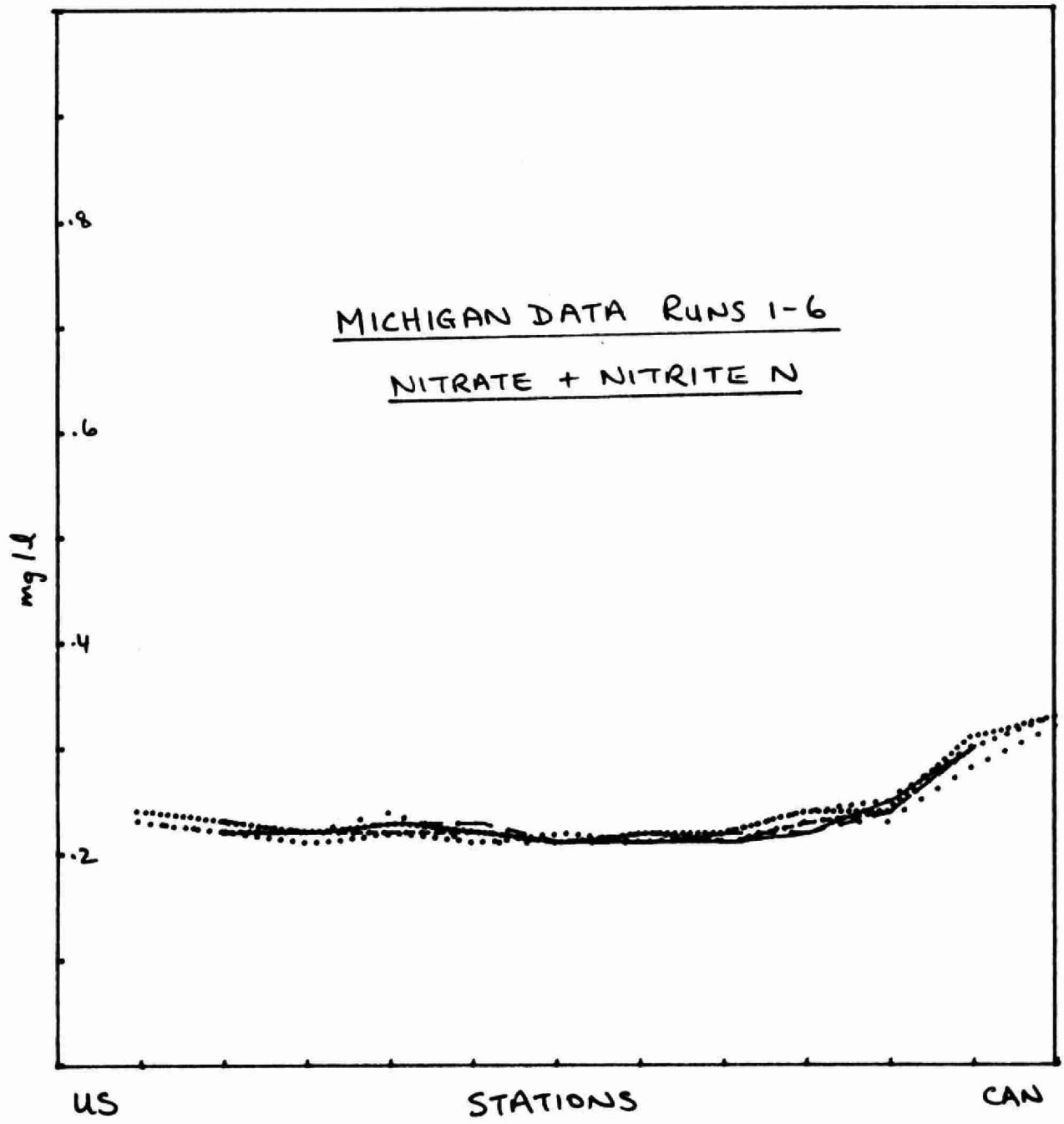

MICHIGAN DATA RUNS 1-6
NITRATE + NITRITE N
mg/l
.8
.6
.4
.2
US
STATIONS
CAN

Figure 3 b)

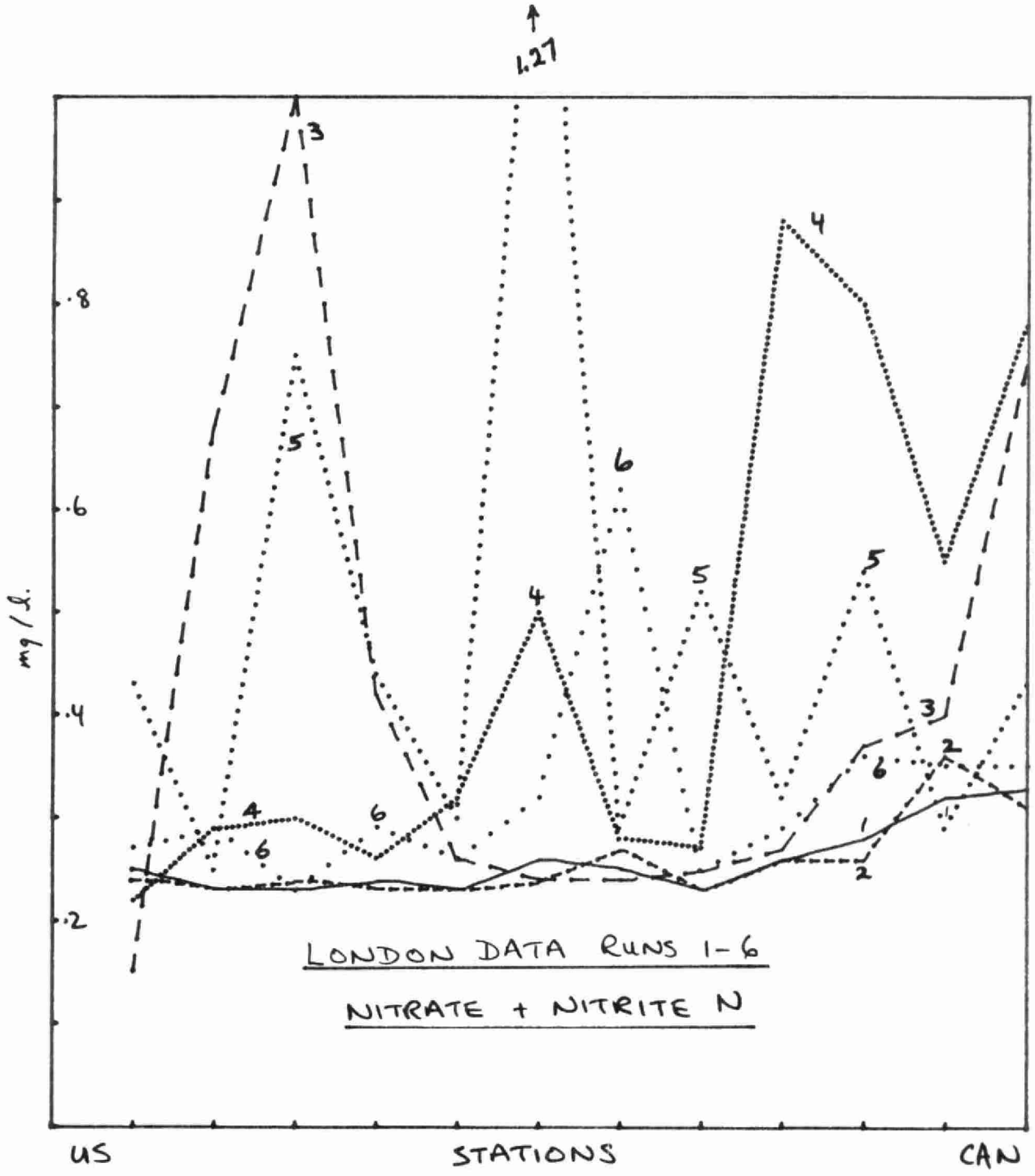

4.27
.8
.6
.4
.2
mg/l.
LONDON DATA RUNS 1-6
NITRATE + NITRITE N
US
STATIONS
CAN

Figure 3c)

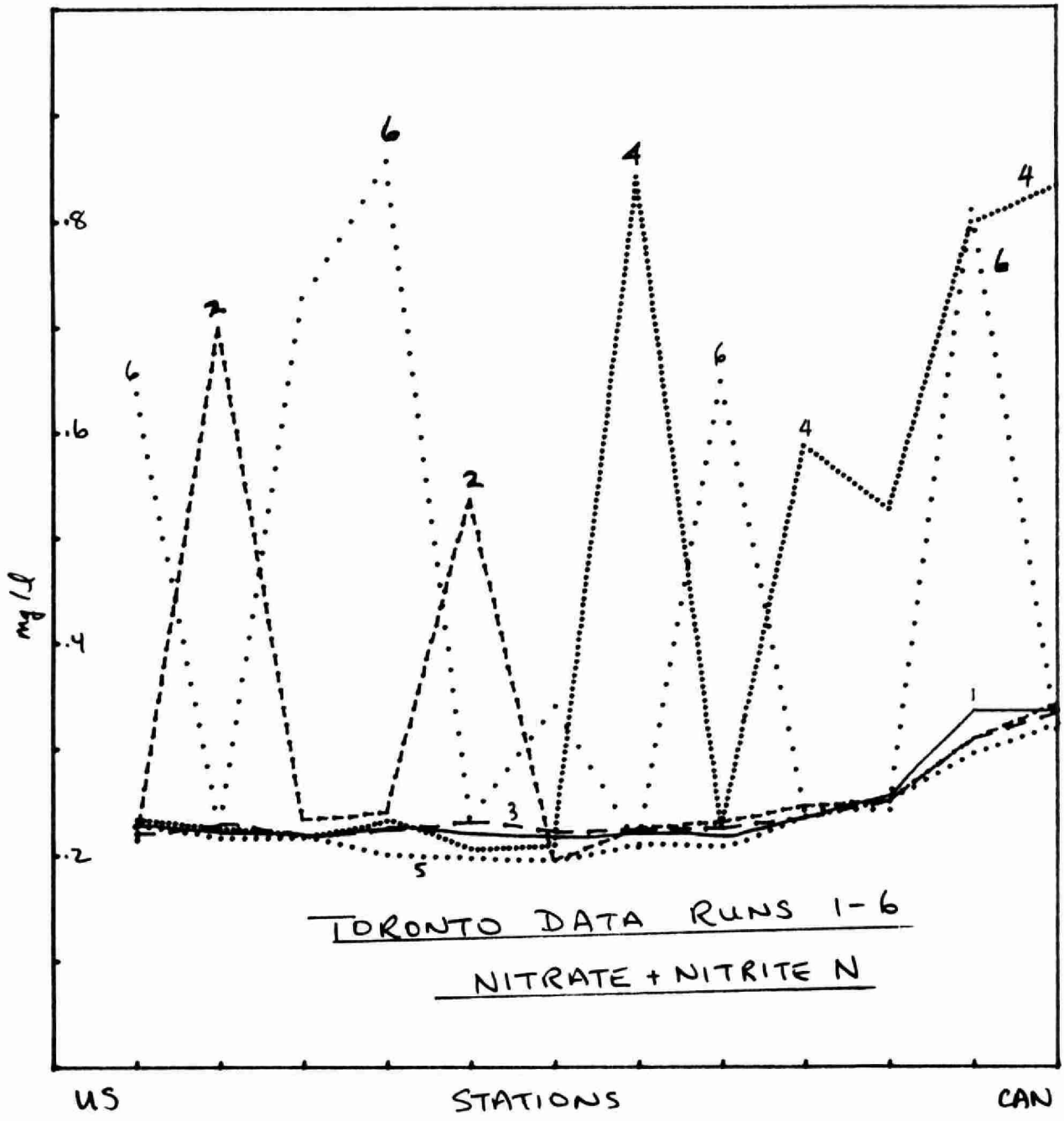

mg/l
.8
.6
.4
.2
6
2
6
2
4
6
4
4
6
1
3
5
TORONTO DATA RUNS 1-6
NITRATE + NITRITE N
US
STATIONS
CAN

Figure 3 d)

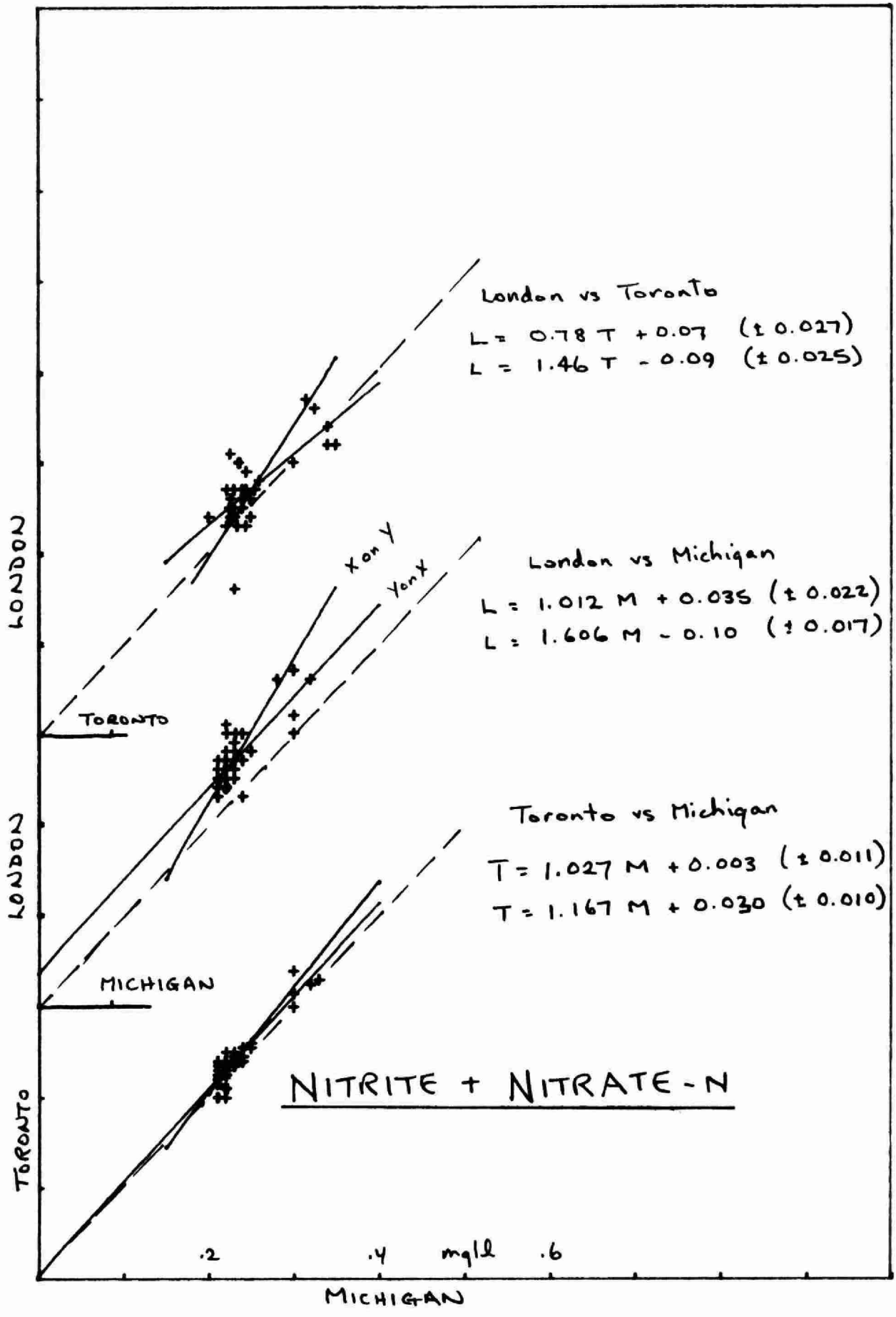
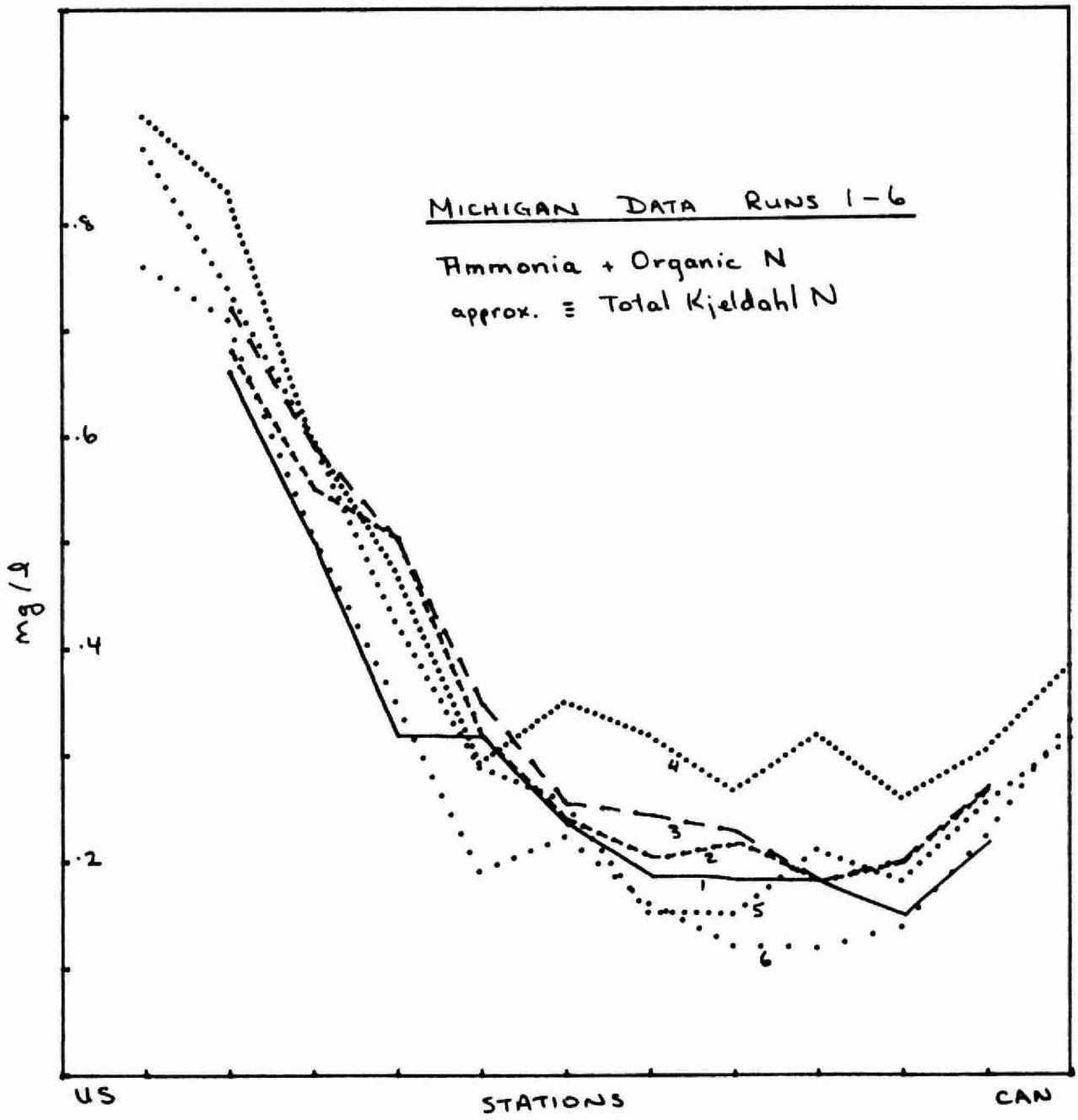

London vs Toronto
L = 0.78 T + 0.07 (± 0.027)
L = 1.46 T - 0.09 (± 0.025)
London vs Michigan
L = 1.012 M + 0.035 (± 0.022)
L = 1.606 M - 0.10 (± 0.017)
Toronto vs Michigan
T = 1.027 M + 0.003 (± 0.011)
T = 1.167 M + 0.030 (± 0.010)
x on y
y on x
TORONTO
MICHIGAN
LONDON
LONDON
TORONTO
NITRITE + NITRATE-N
.2
.4
mg/l
.6
MICHIGAN

Figure 4 a)



MICH TKN

Figure 4 b)

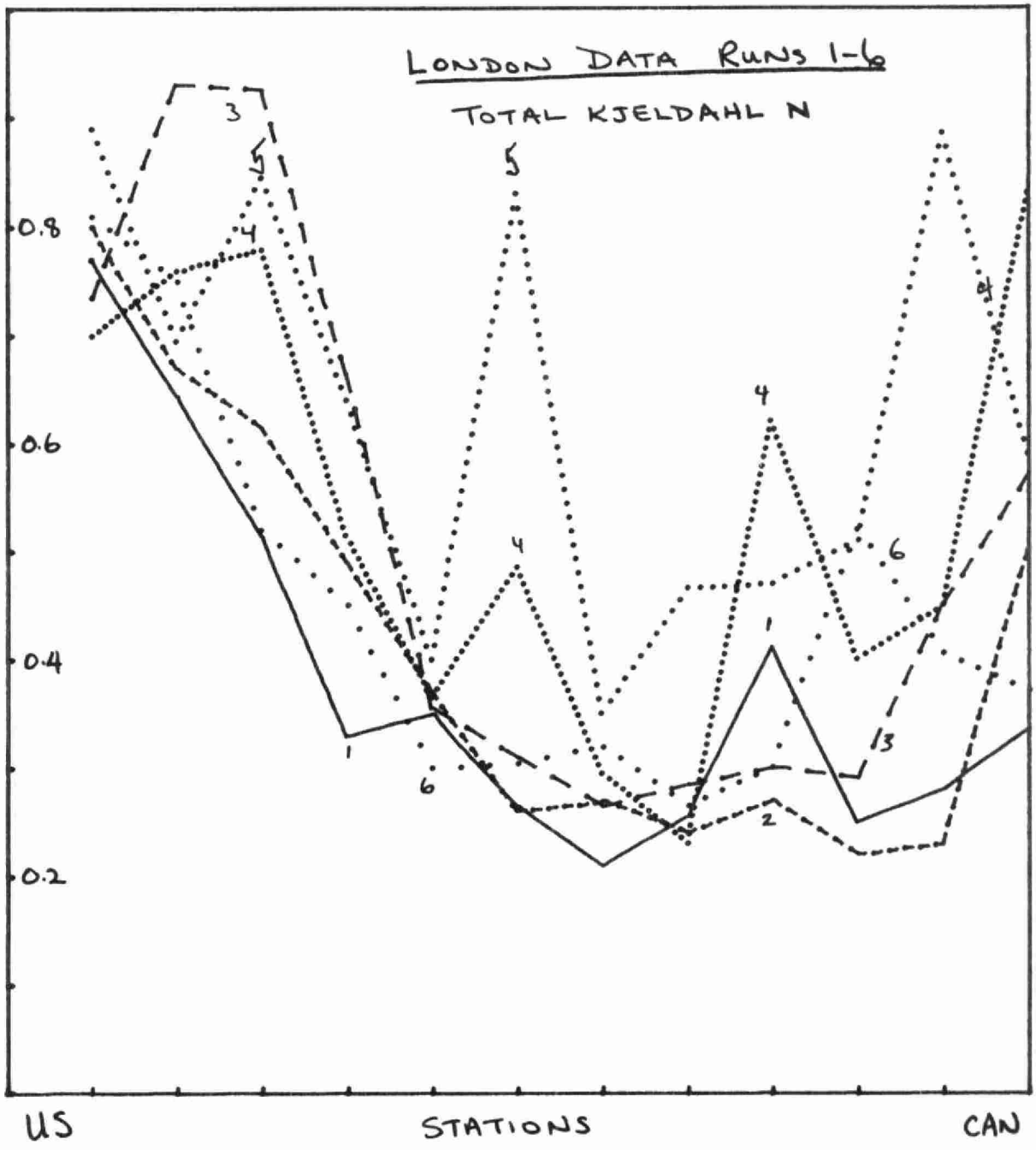

LONDON DATA RUNS 1-6
TOTAL KJELDAHL N
0.8
0.6
0.4
0.2
US
STATIONS
CAN

Figure 4c

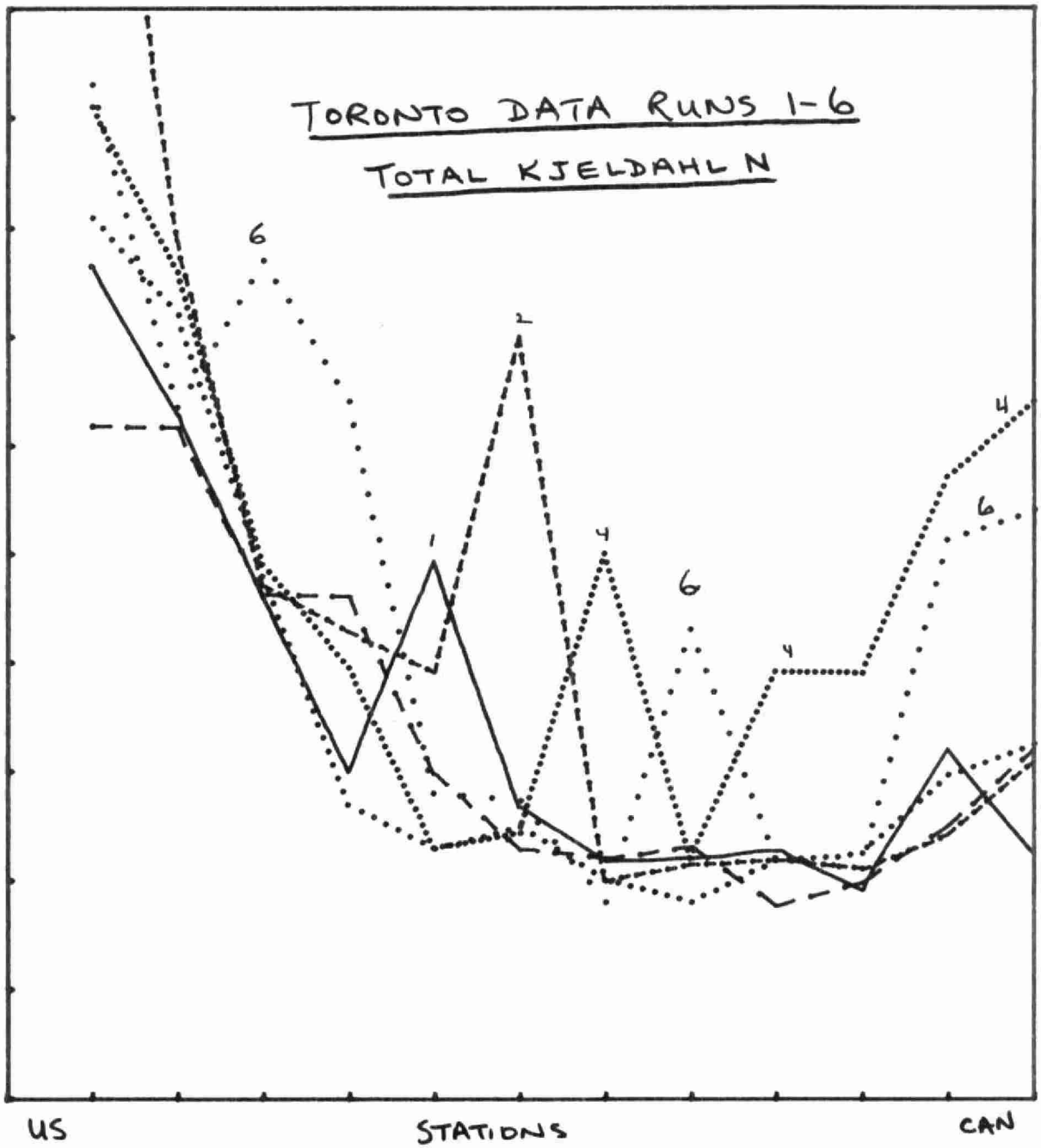


Figure 4d)

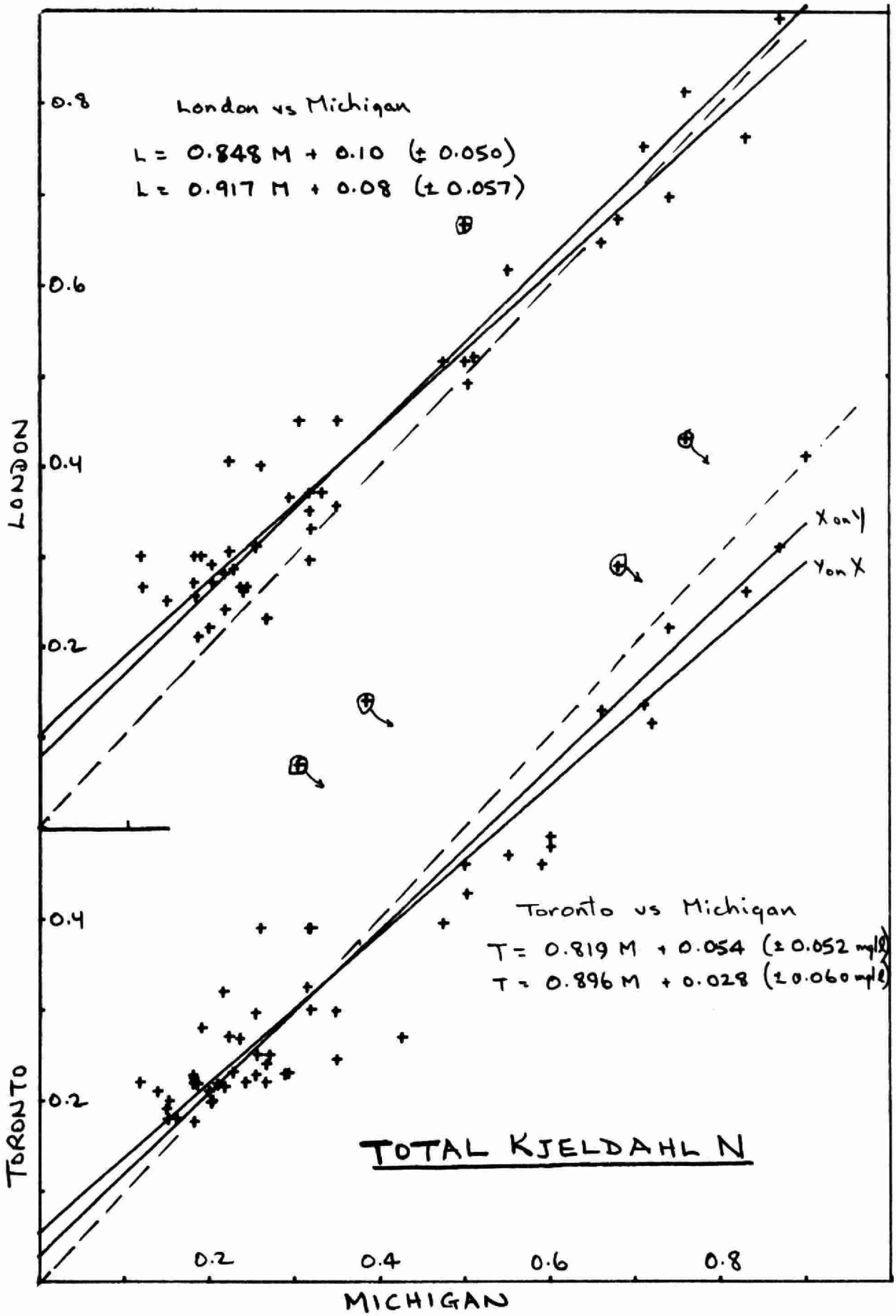

London vs Michigan
L = 0.848 M + 0.10 (± 0.050)
L = 0.917 M + 0.08 (± 0.057)
X on Y
Y on X
Toronto vs Michigan
T = 0.819 M + 0.054 (± 0.052 mg/l)
T = 0.896 M + 0.028 (± 0.060 mg/l)
TOTAL KJELDAHL N
LONDON
TORONTO
MICHIGAN
0.2
0.4
0.6
0.8

Figure 4 d) continued

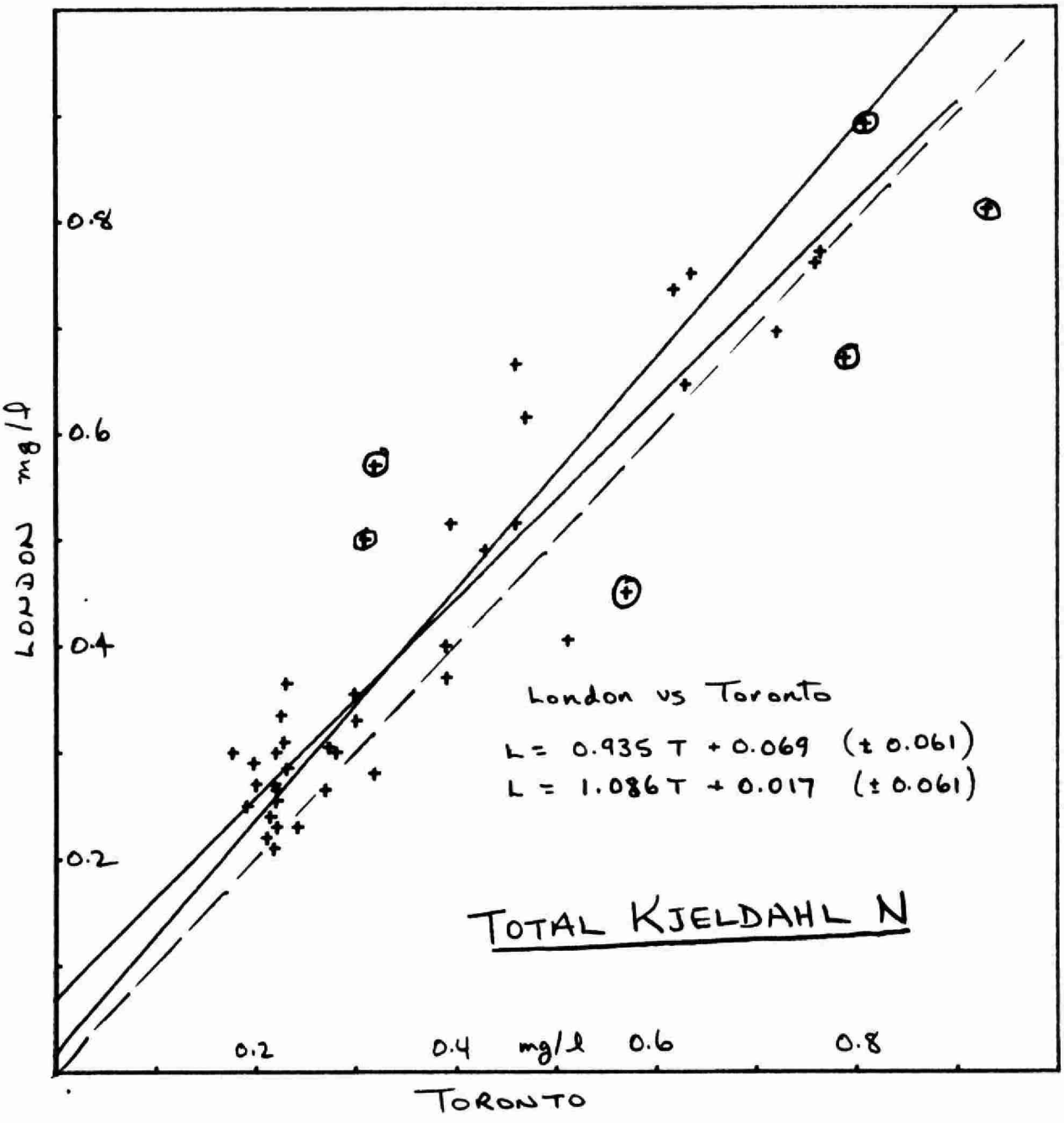


Figure 5 a)

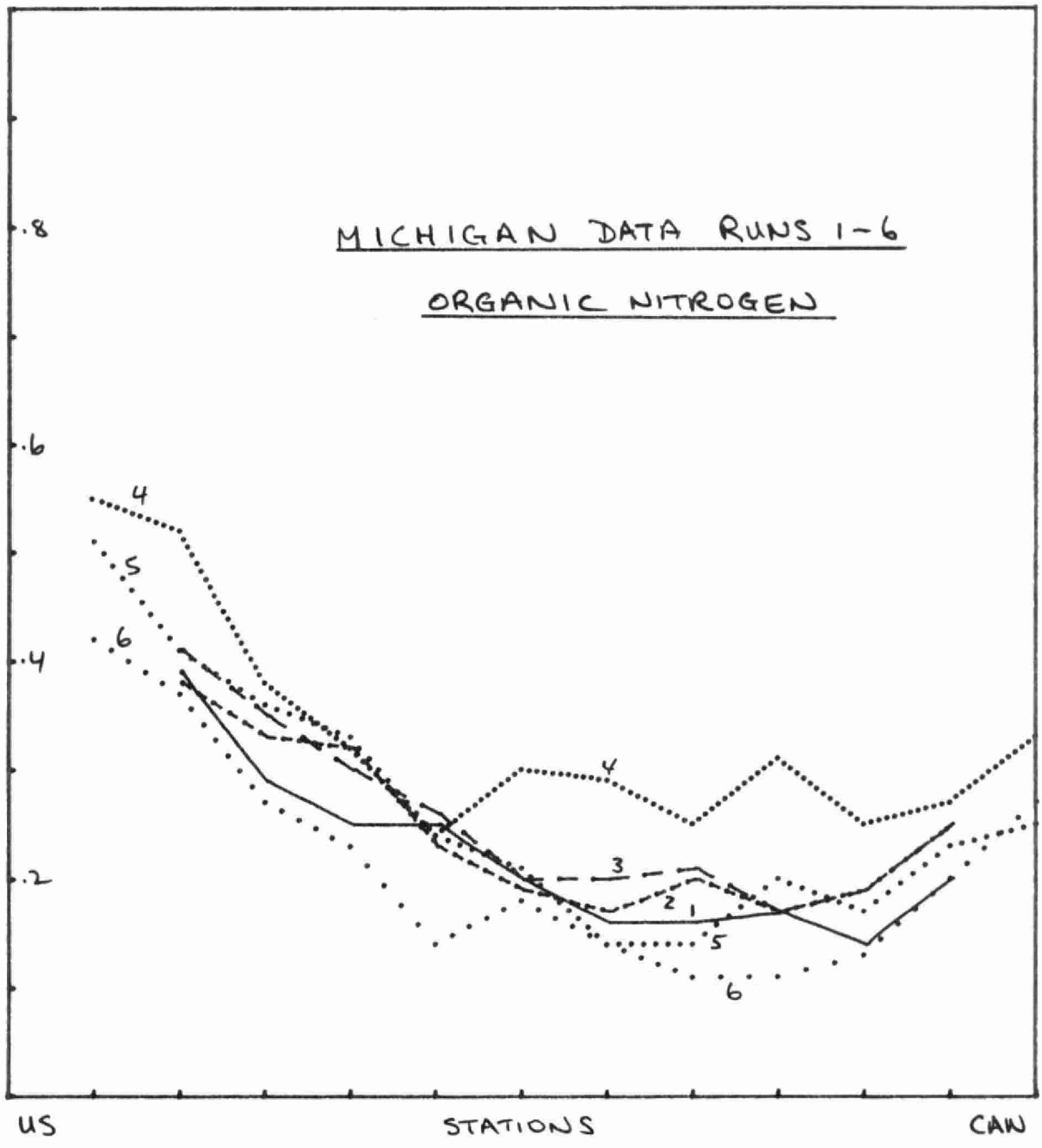

MICHIGAN DATA RUNS 1-6
ORGANIC NITROGEN
.8
.6
.4
.2
4
5
6
4
3
2
1
5
6
US
STATIONS
CAN

Figure 5b)

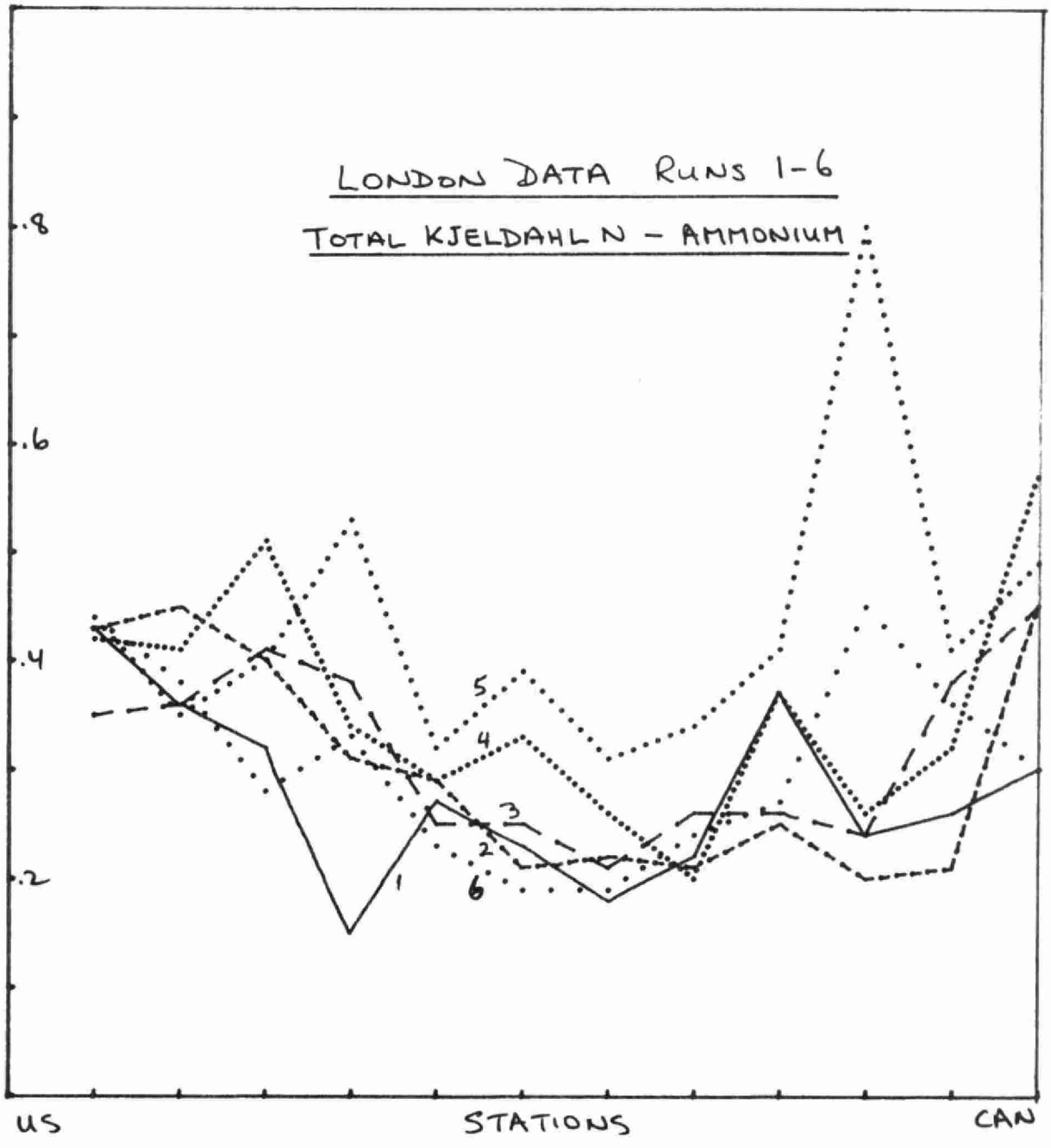
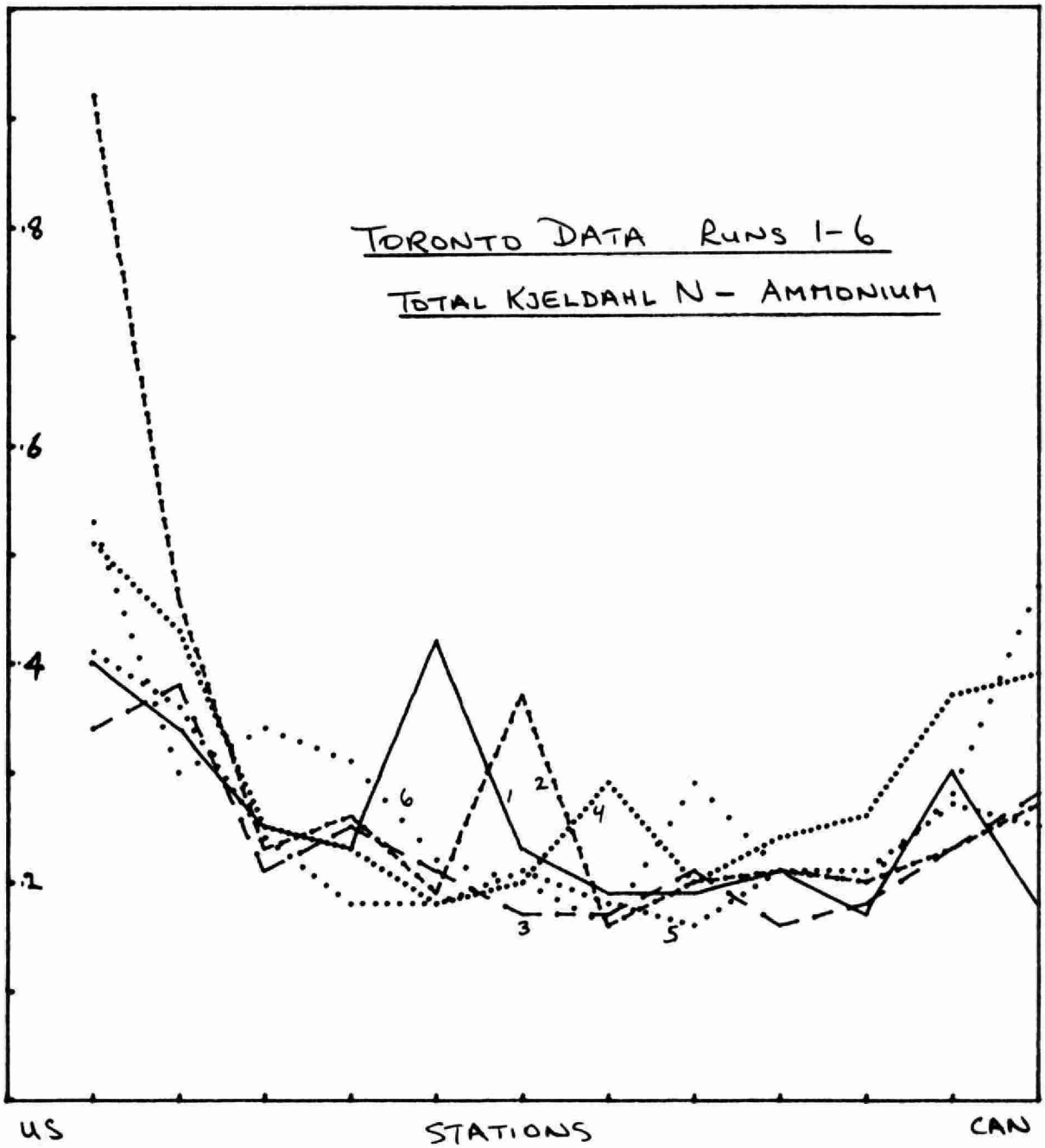

LONDON DATA RUNS 1-6
TOTAL KJELDAHL N - AMMONIUM
.8
.6
.4
.2
1
2
3
4
5
6
US
STATIONS
CAN

Figure 5 c)



T ON 1

Figure 5d)

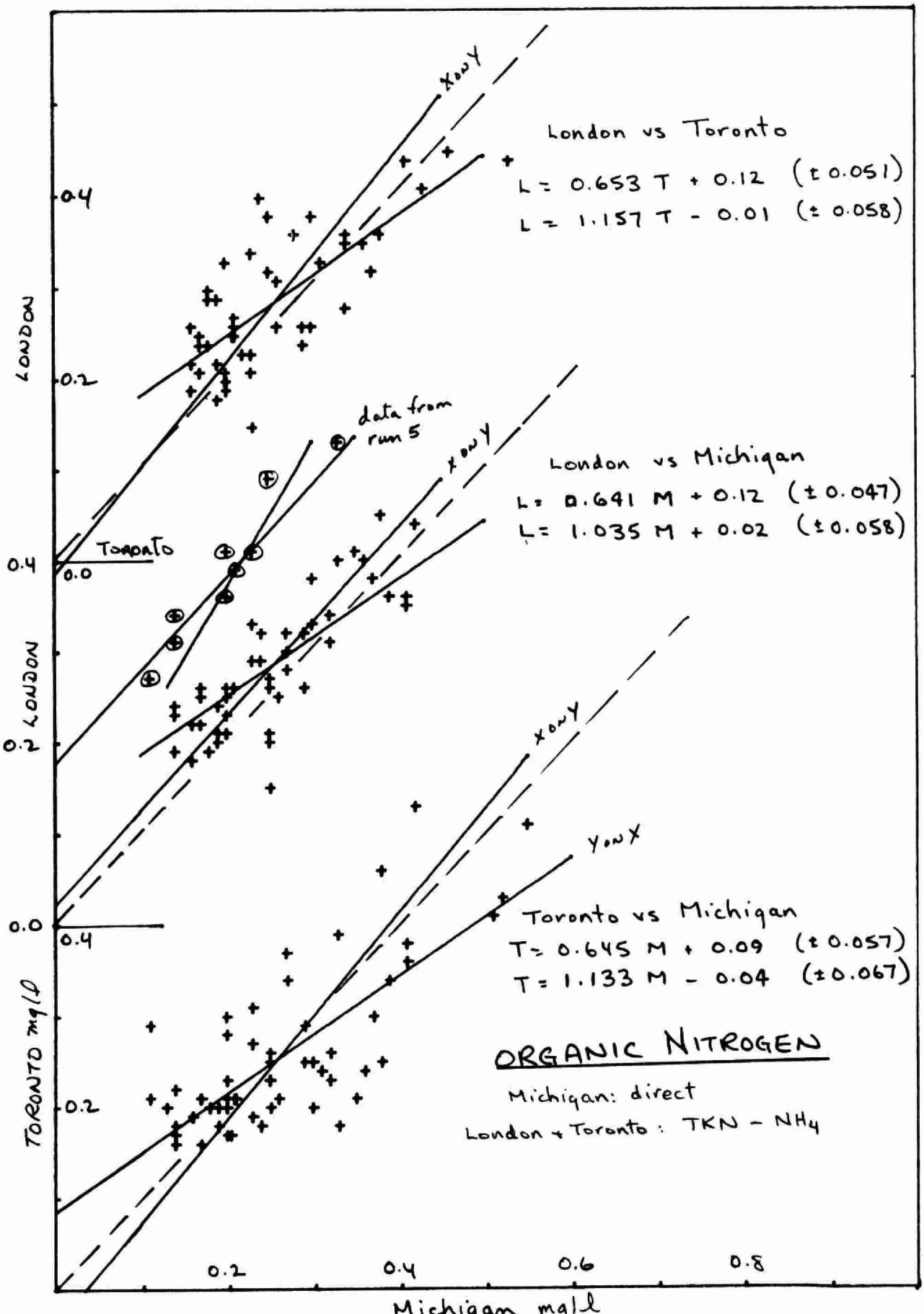

London vs Toronto
L = 0.653 T + 0.12 (± 0.051)
L = 1.157 T - 0.01 (± 0.058)
London vs Michigan
L = 0.641 M + 0.12 (± 0.047)
L = 1.035 M + 0.02 (± 0.058)
Toronto vs Michigan
T = 0.645 M + 0.09 (± 0.057)
T = 1.133 M - 0.04 (± 0.067)
ORGANIC NITROGEN
Michigan: direct
London + Toronto: TKN - NH4
x on Y
y on x
data from run 5
Toronto
LONDON
TORONTO mg/l
Michigan mg/l
0.0
0.2
0.4
0.6
0.8

Figure 6a)

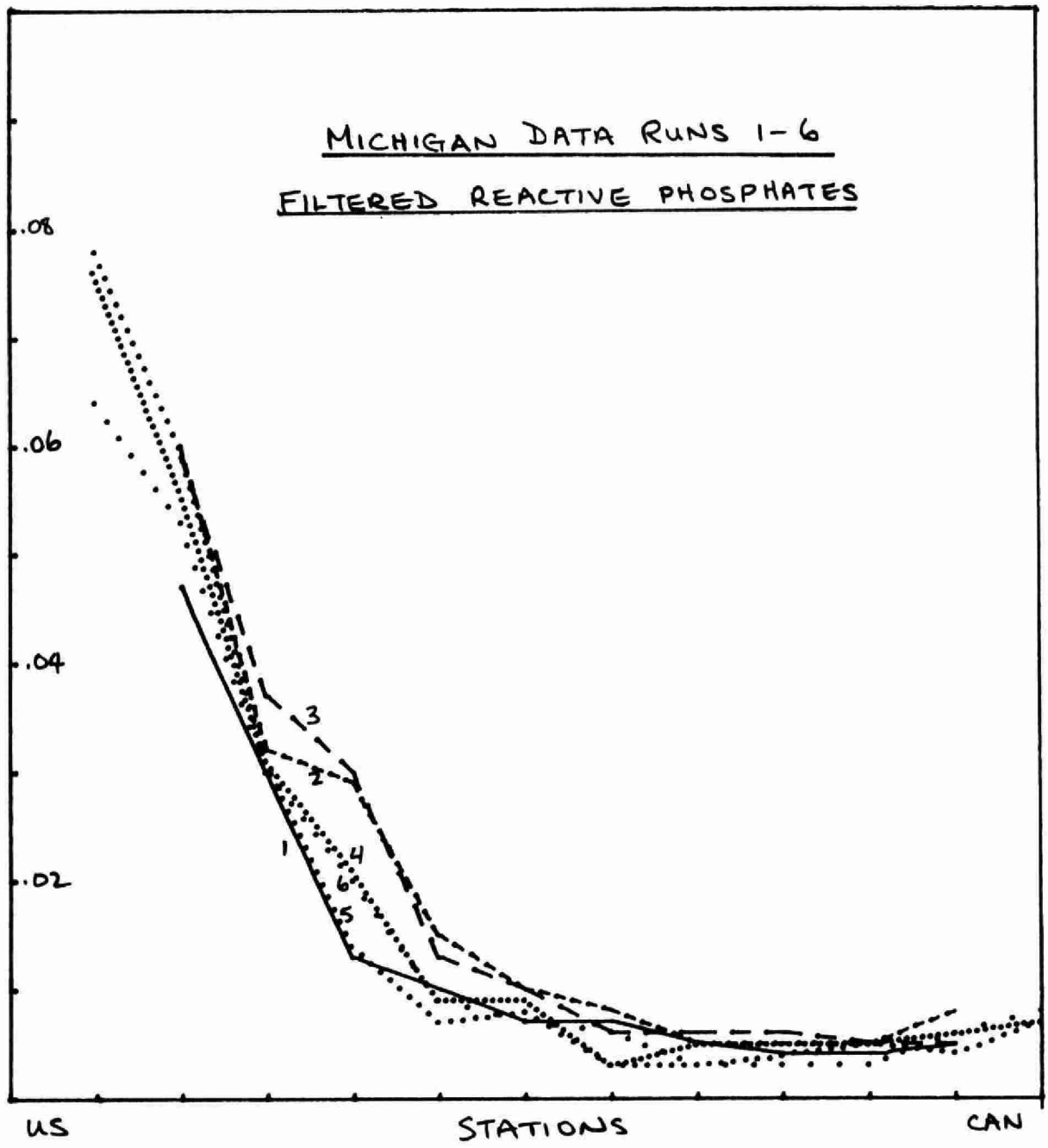

MICHIGAN DATA RUNS 1-6
FILTERED REACTIVE PHOSPHATES
.08
.06
.04
.02
1
2
3
4
5
6
US
STATIONS
CAN

Figure 6 b)

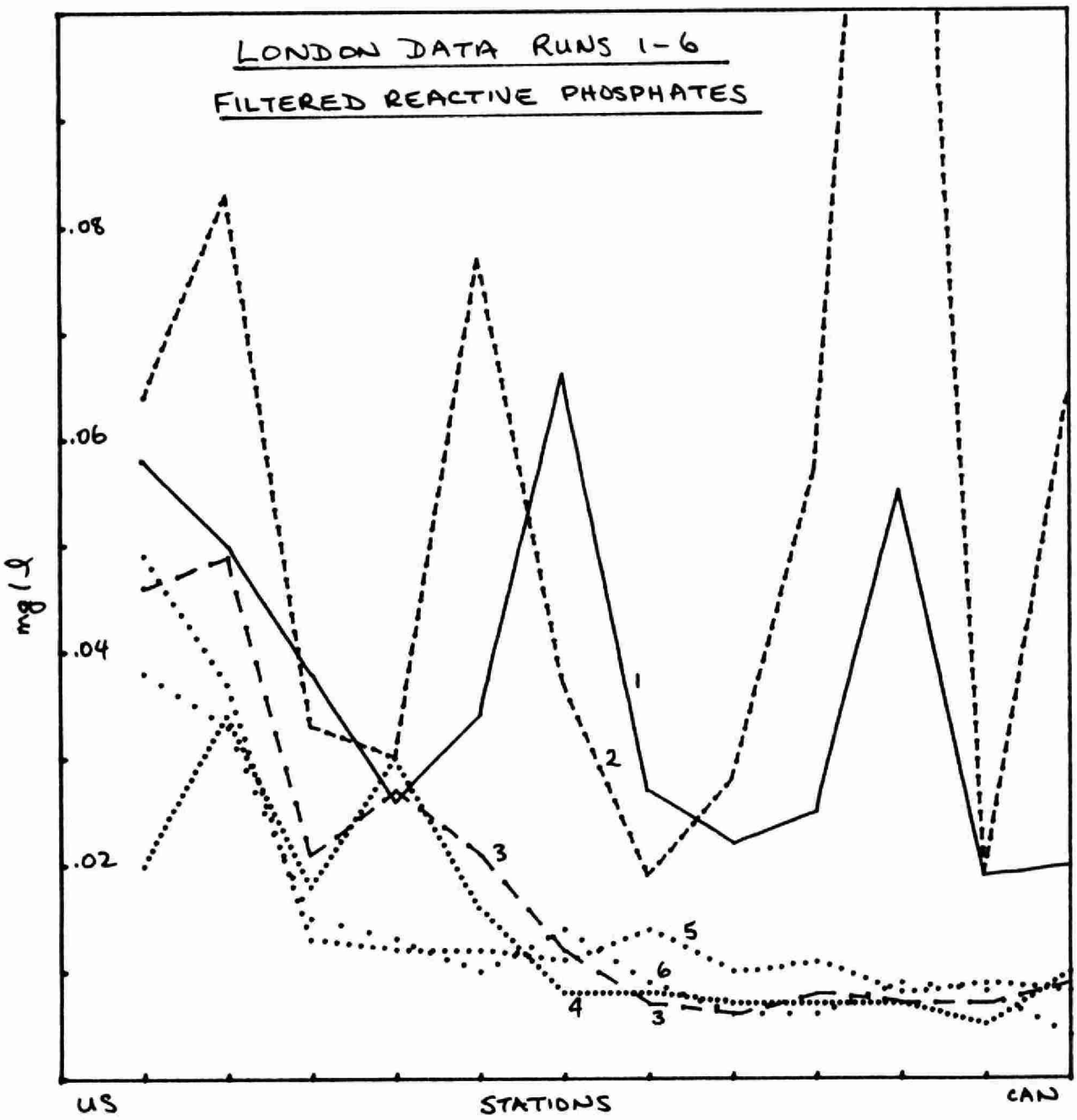
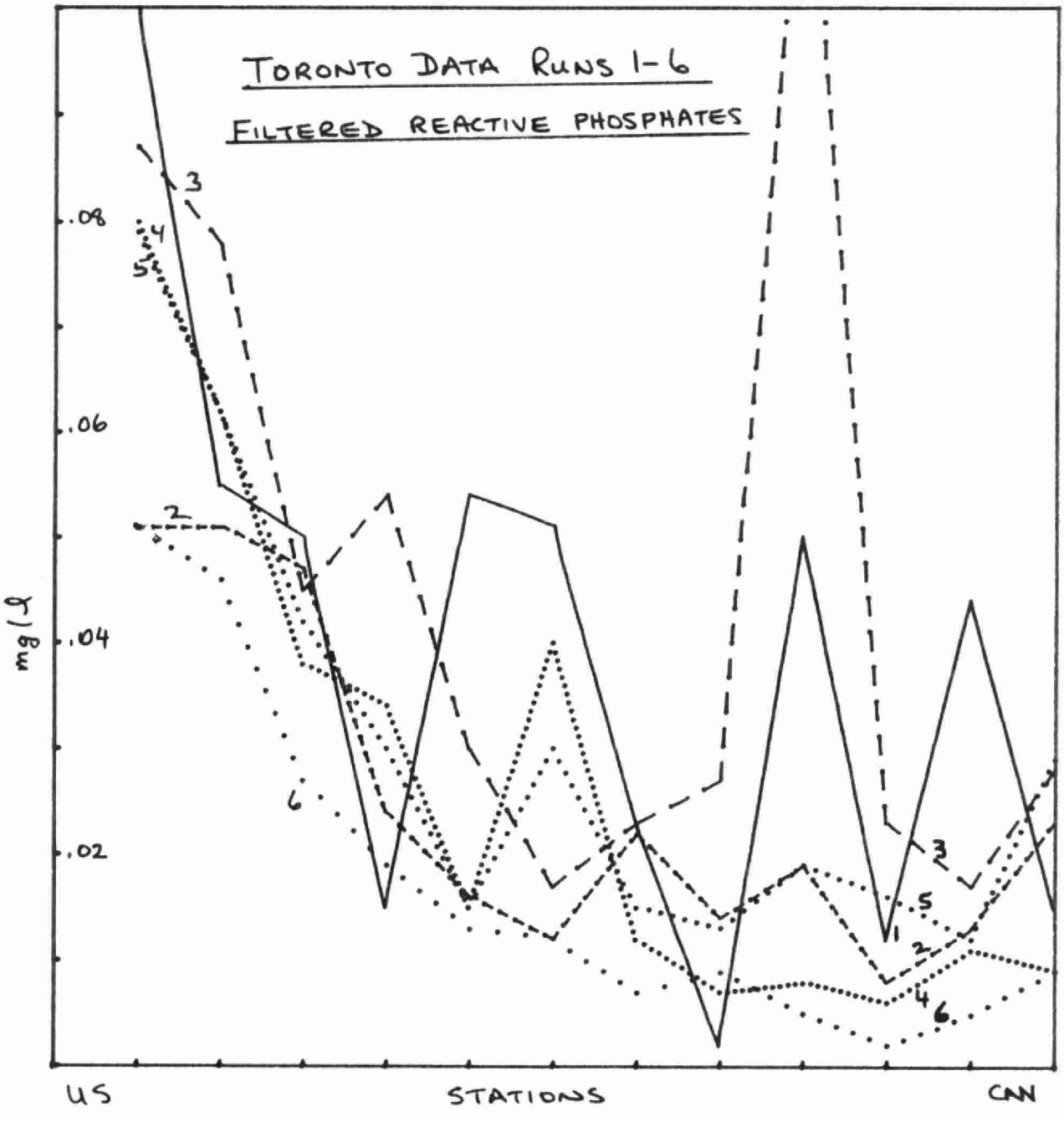

LONDON DATA RUNS 1-6
FILTERED REACTIVE PHOSPHATES
.08
.06
.04
.02
mg/l
1
2
3
4
5
6
3
US
STATIONS
CAN

Figure 6c)



T PO4 .1

Figure 6 d)

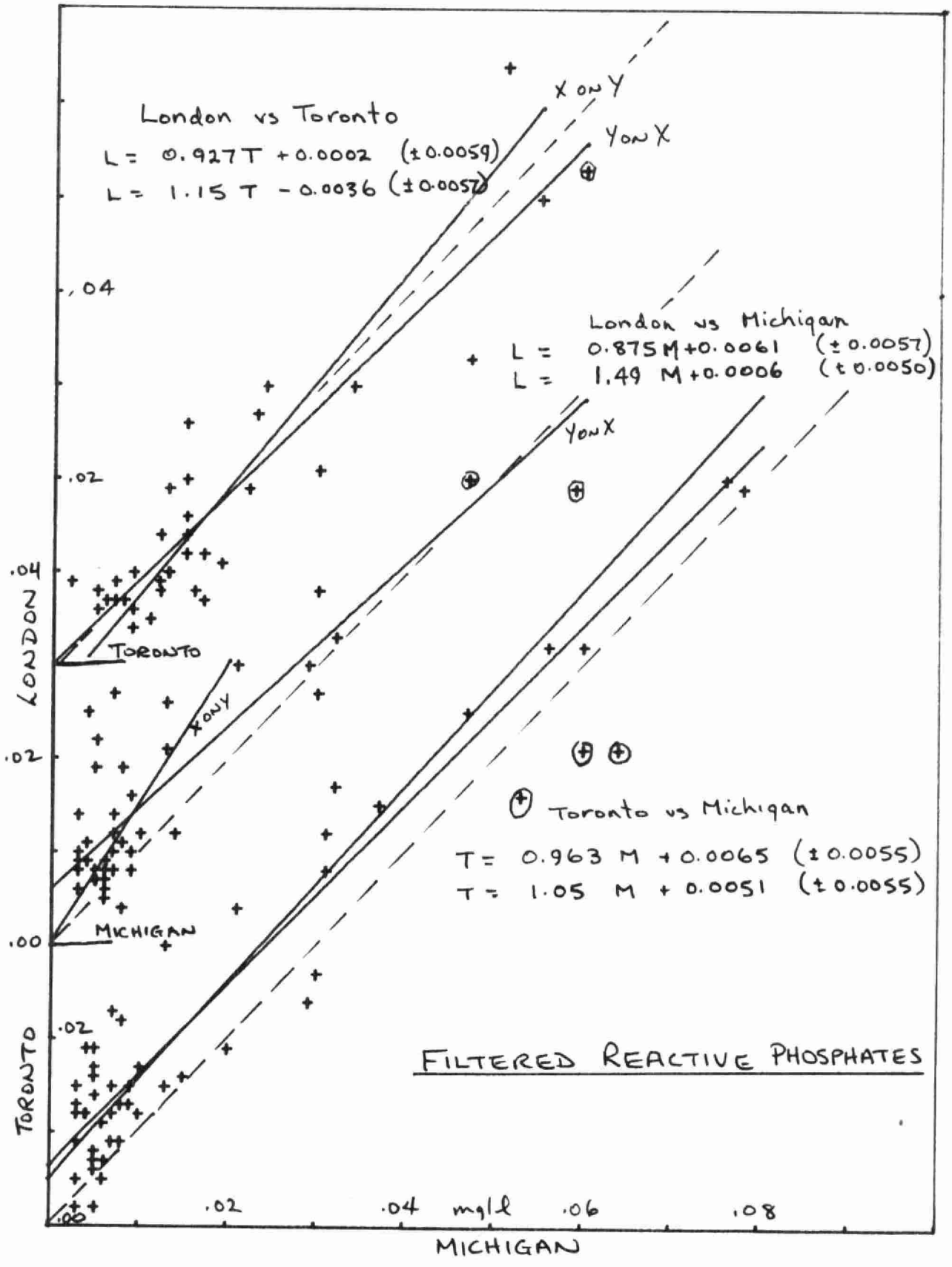

London vs Toronto
L = 0.927T + 0.0002 (±0.0059)
L = 1.15 T - 0.0036 (±0.0057)
X on Y
Y on X
London vs Michigan
L = 0.875M + 0.0061 (±0.0057)
L = 1.49 M + 0.0006 (±0.0050)
Y on X
Toronto vs Michigan
T = 0.963 M + 0.0065 (±0.0055)
T = 1.05 M + 0.0051 (±0.0055)
TORONTO
X ONLY
MICHIGAN
LONDON
TORONTO
MICHIGAN
.04
.02
.00
.02
.02
.04
.06
.08
mg/l
FILTERED REACTIVE PHOSPHATES

Figure 7a)

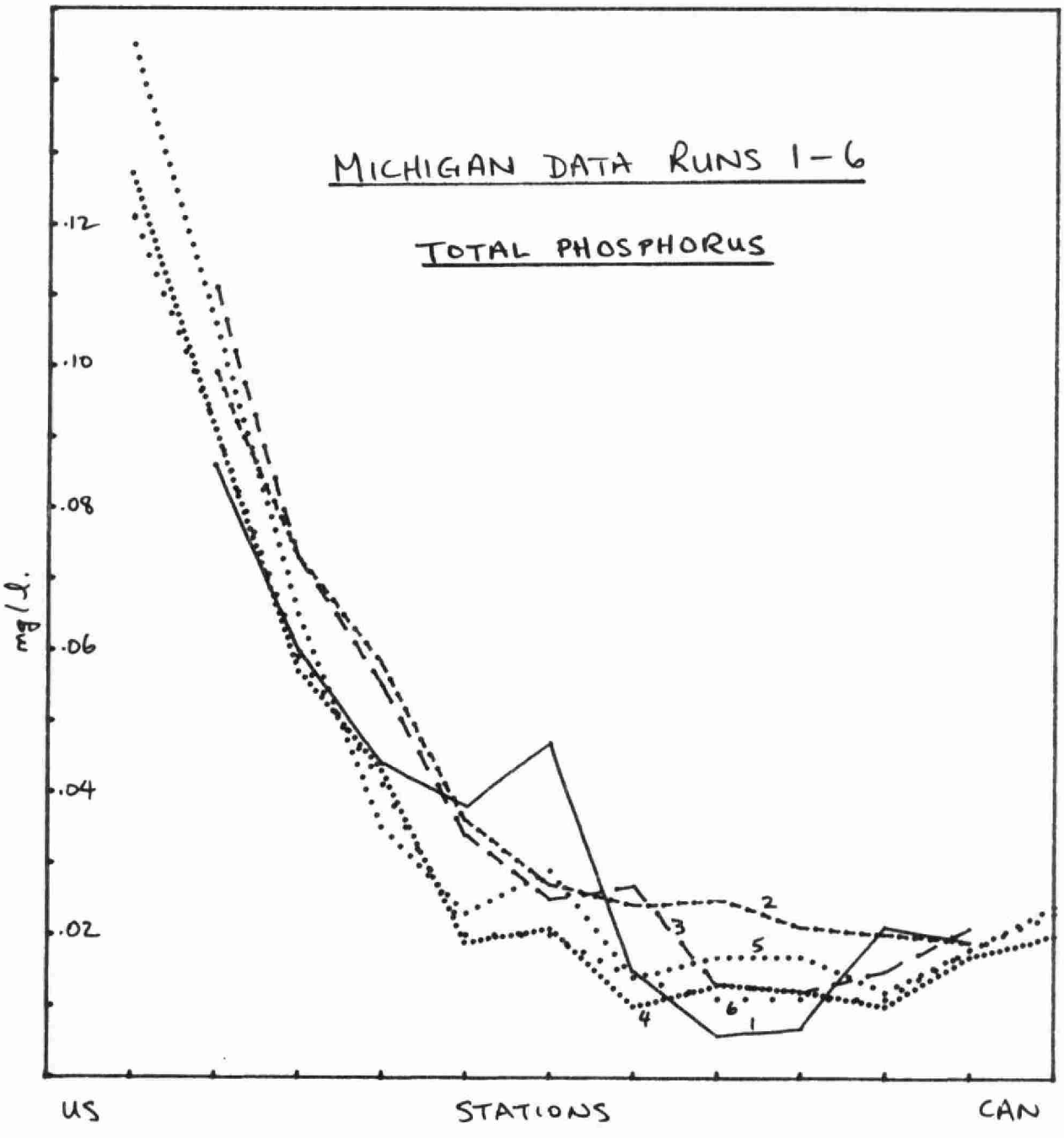

MICHIGAN DATA RUNS 1-6
TOTAL PHOSPHORUS
.12
.10
.08
.06
.04
.02
mg/l P
US
STATIONS
CAN
1
2
3
4
5
6

Figure 7b

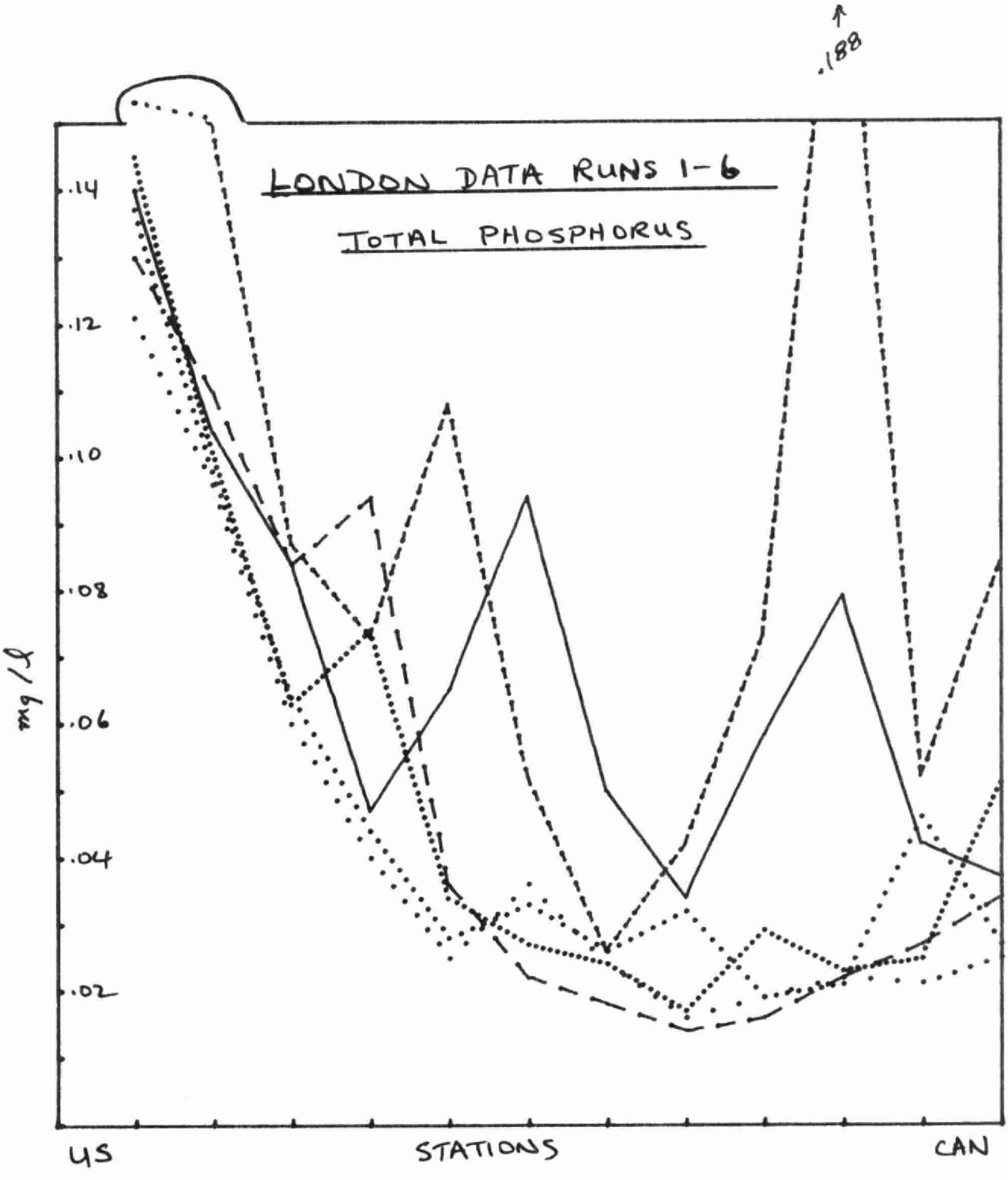
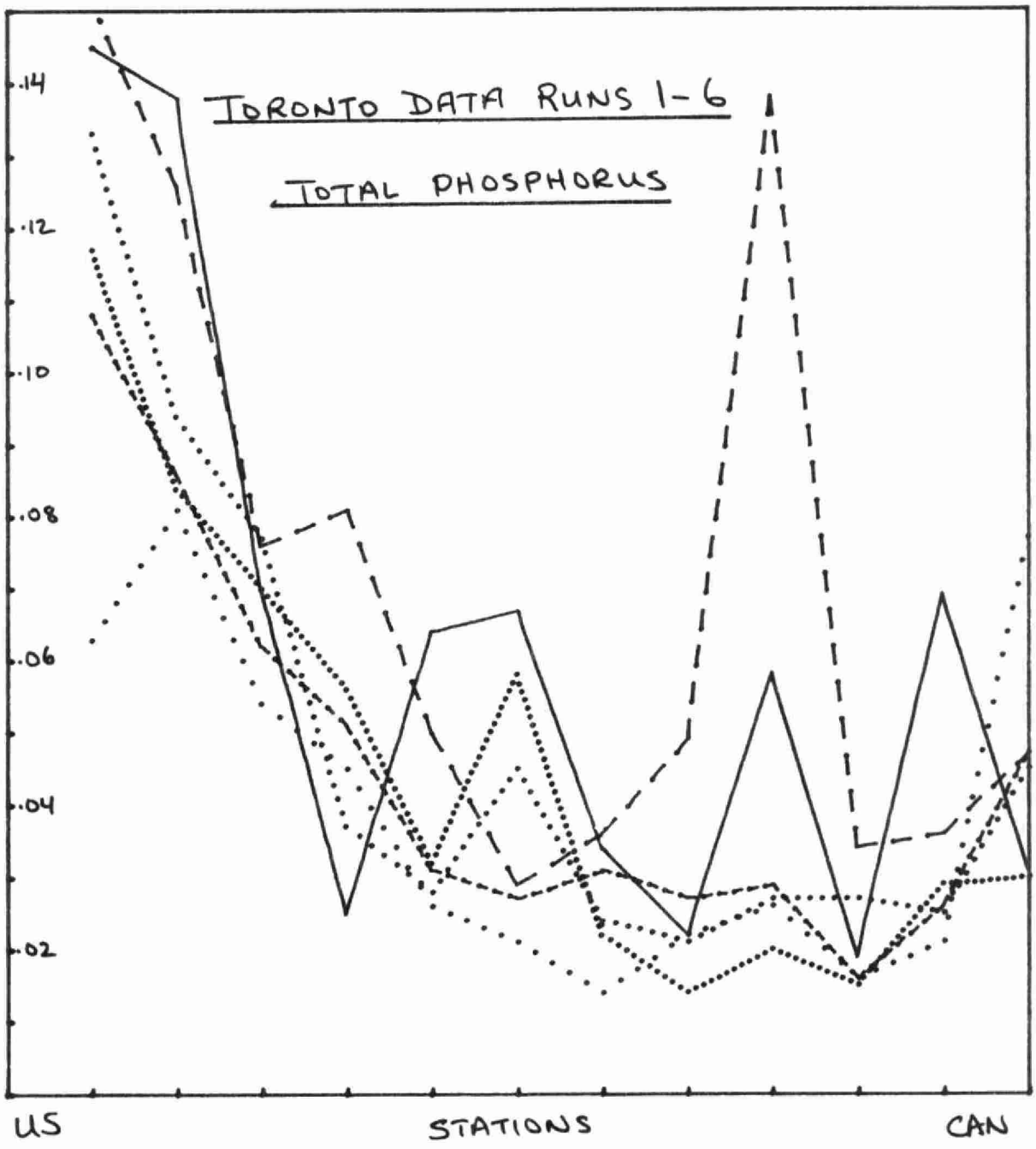

.188
LONDON DATA RUNS 1-6
TOTAL PHOSPHORUS
.14
.12
.10
.08
.06
.04
.02
mg/l
US
STATIONS
CAN

Figure 7c)



T TP .15

Figure 7d)

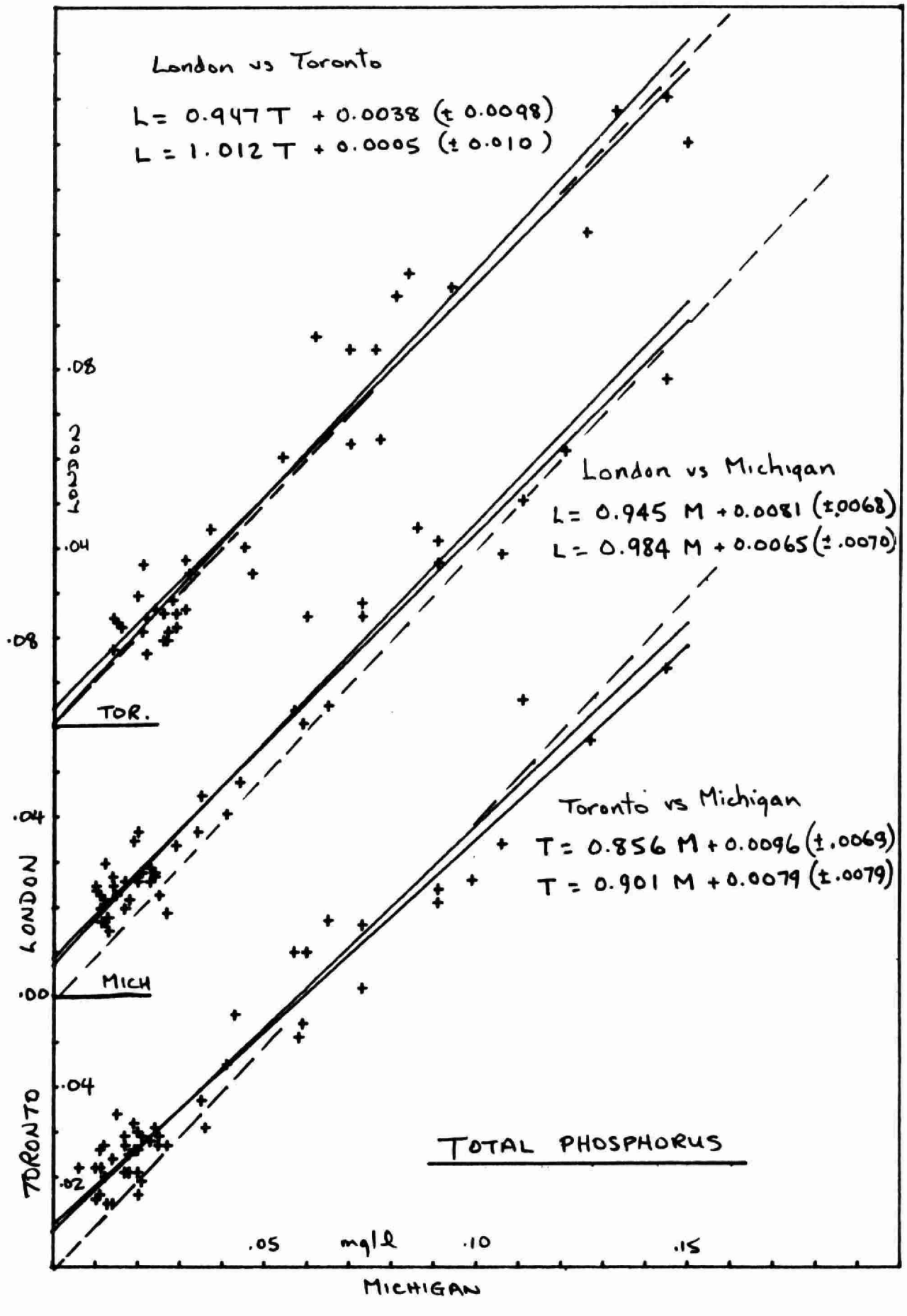
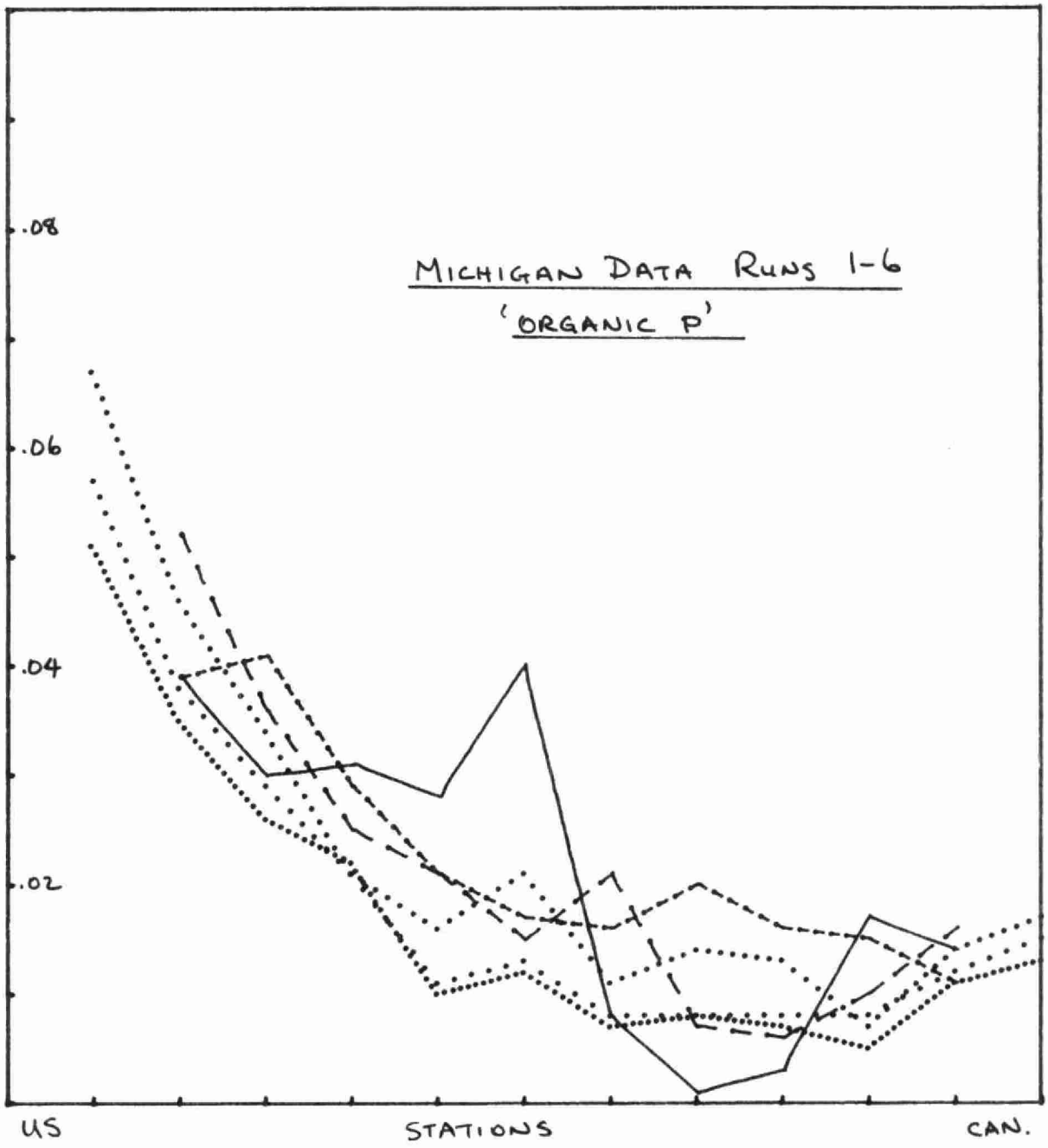

London vs Toronto
L = 0.947 T + 0.0038 (± 0.0098)
L = 1.012 T + 0.0005 (± 0.010)
London vs Michigan
L = 0.945 M + 0.0081 (±.0068)
L = 0.984 M + 0.0065 (±.0070)
Toronto vs Michigan
T = 0.856 M + 0.0096 (±.0069)
T = 0.901 M + 0.0079 (±.0079)
TOTAL PHOSPHORUS
LONDON
TORONTO
MICHIGAN
TOR.
MICH
.08
.04
.00
.02
.05
.10
.15
mg/l

Figure 8a)



MDP-1

Figure 8b)

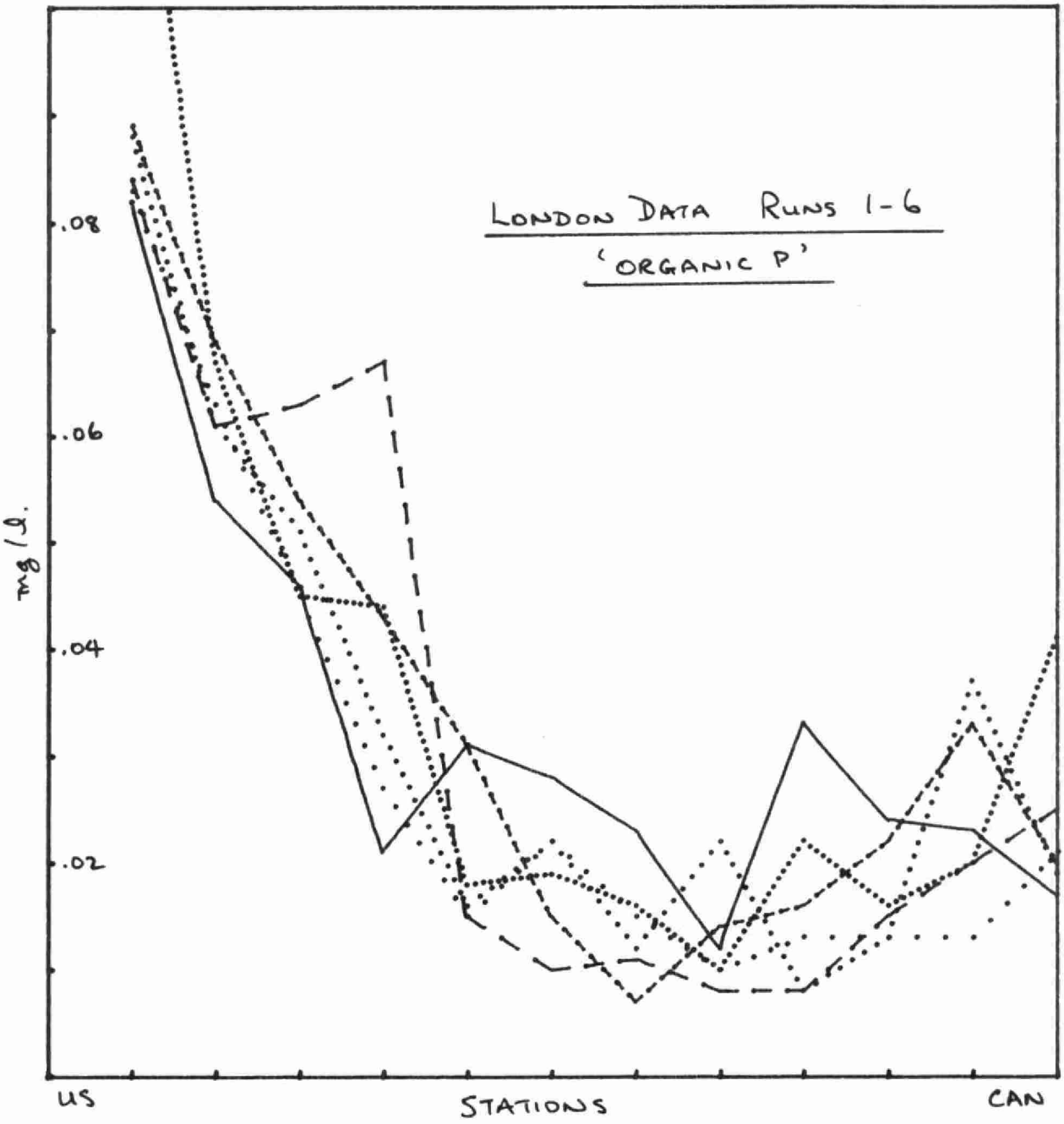


Figure 8c

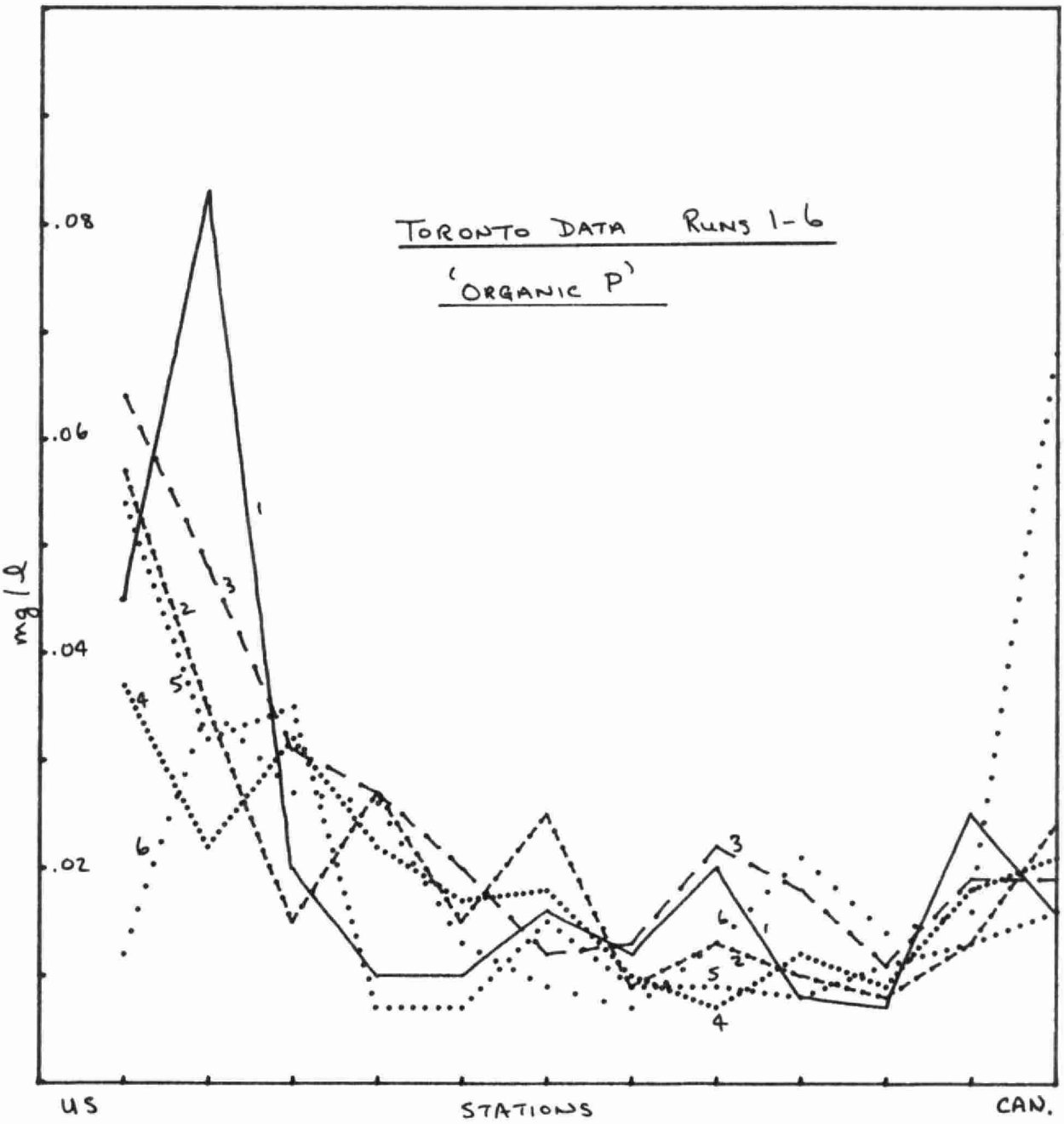


Figure 8a)

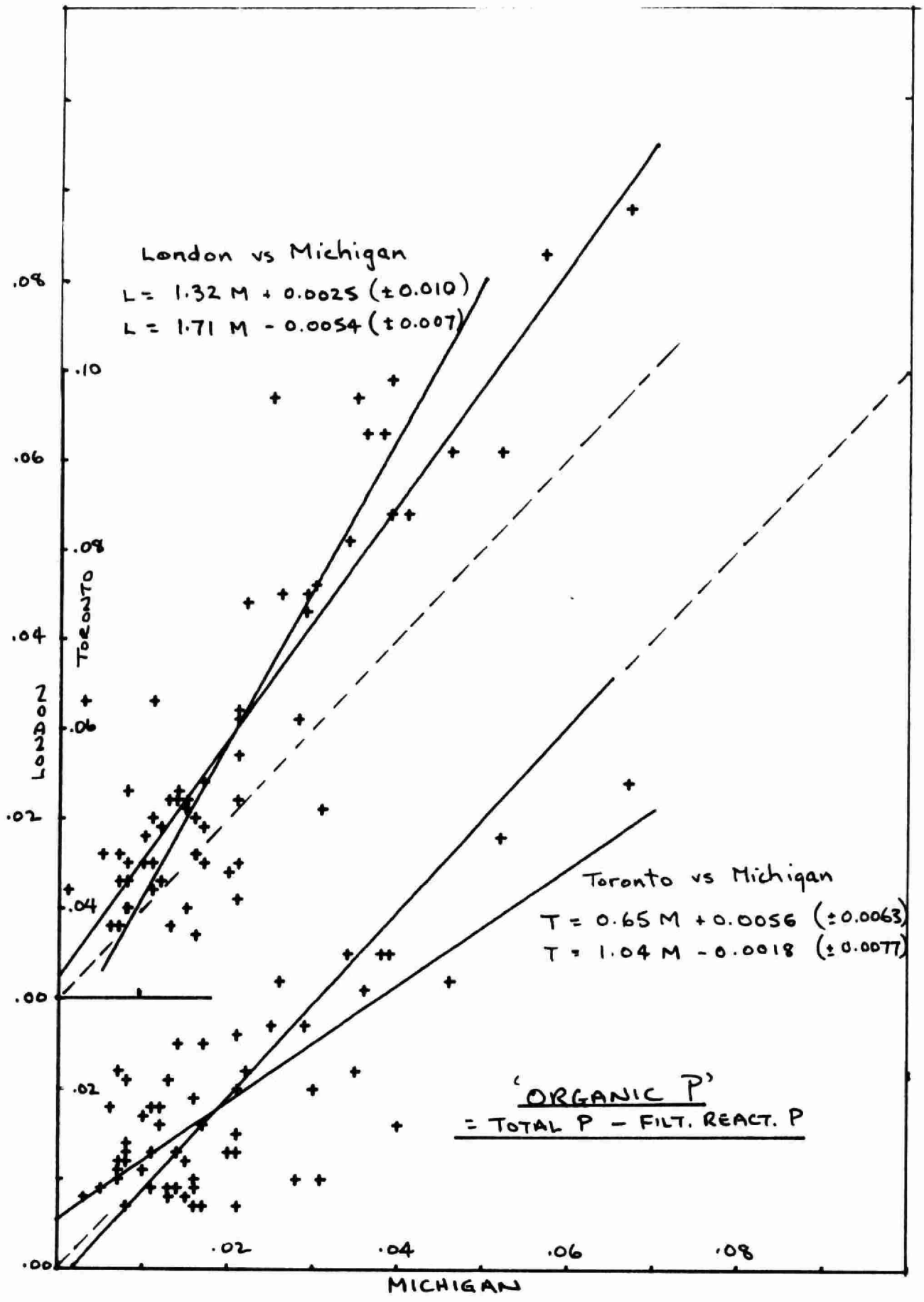

London vs Michigan
L = 1.32 M + 0.0025 (±0.010)
L = 1.71 M - 0.0054 (±0.007)
Toronto vs Michigan
T = 0.65 M + 0.0056 (±0.0063)
T = 1.04 M - 0.0018 (±0.0077)
'ORGANIC P'
= TOTAL P - FILT. REACT. P
LONDON
TORONTO
MICHIGAN
.00
.02
.04
.06
.08
.10

Figure 8 d) continued

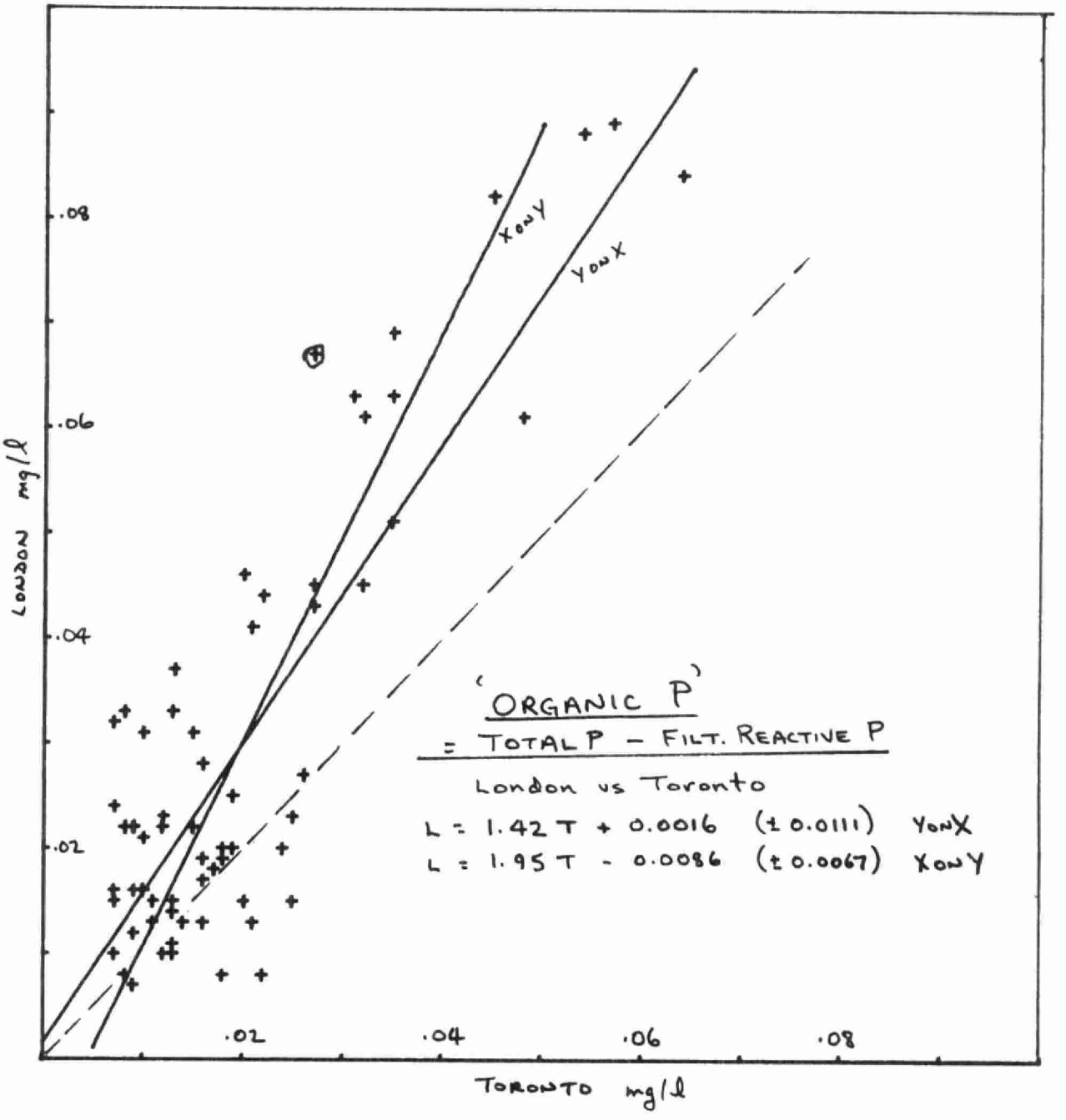


FIGURE 1 to show that the contaminant found in Ontario samples contains 3 nitrate per unit of ammonium as N.

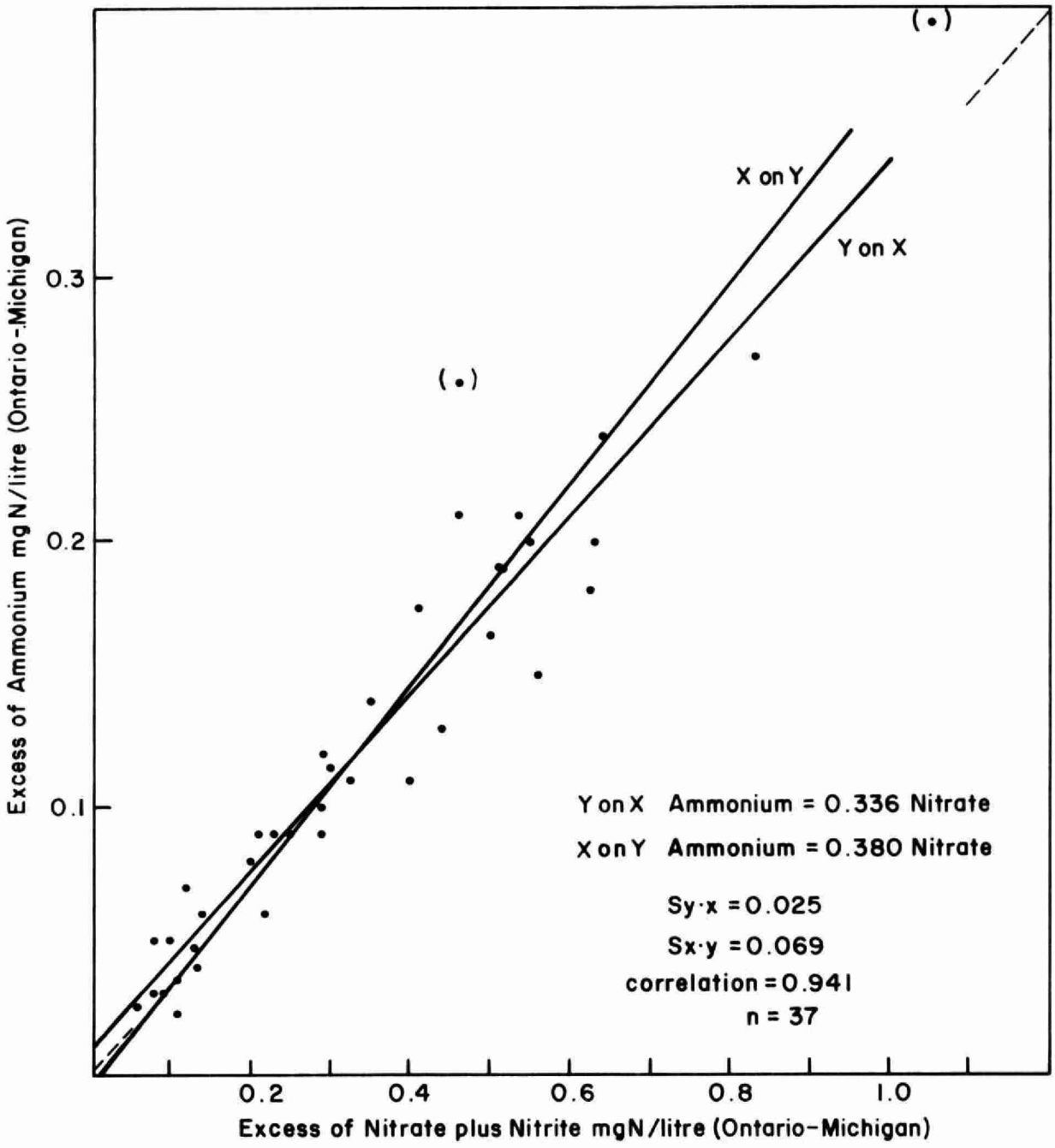


FIGURE 2

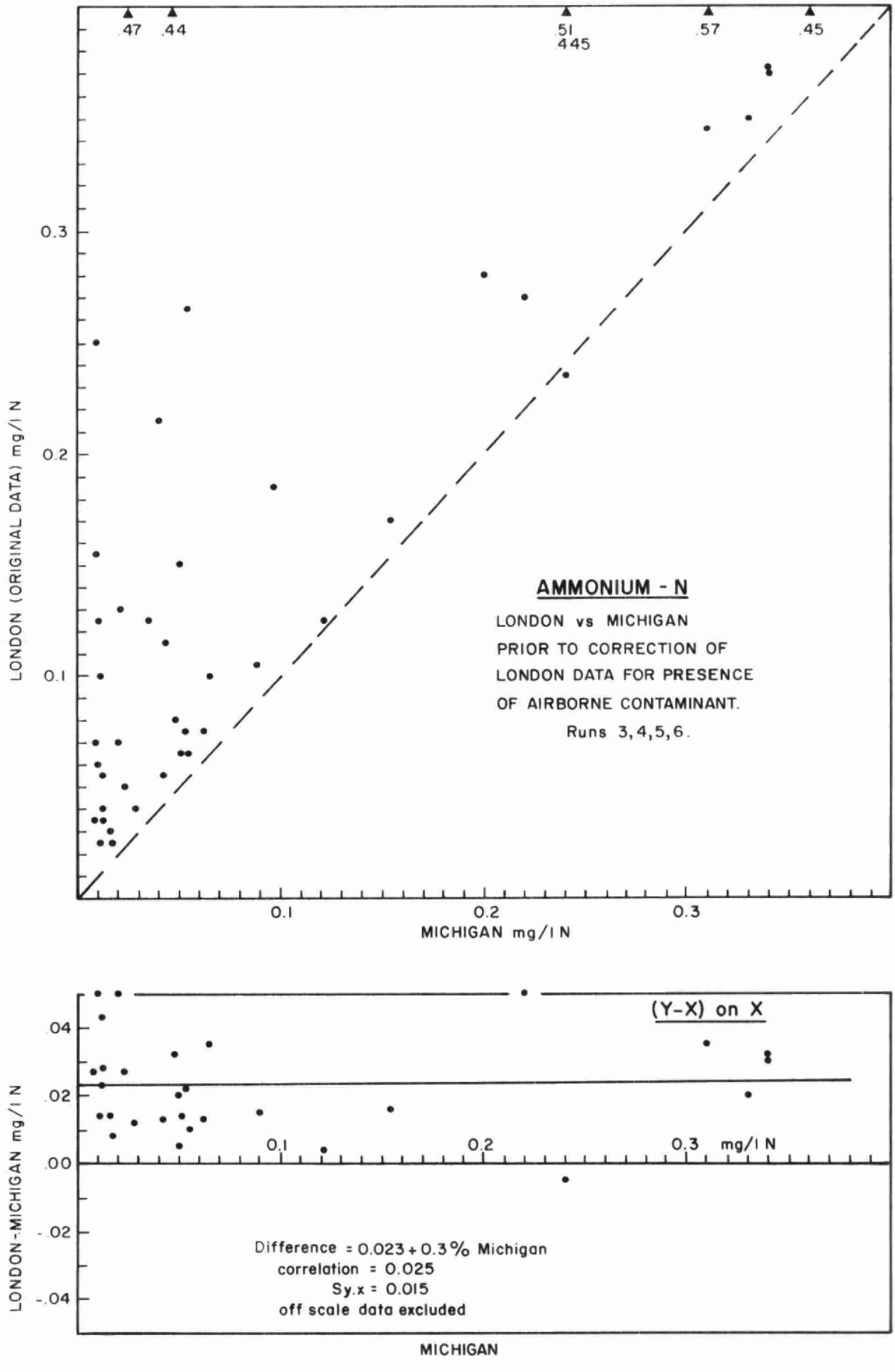

.47
.44
.51
.445
.57
.45
0.3
0.2
0.1
LONDON (ORIGINAL DATA) mg/l N
AMMONIUM - N
LONDON vs MICHIGAN
PRIOR TO CORRECTION OF
LONDON DATA FOR PRESENCE
OF AIRBORNE CONTAMINANT.
Runs 3,4,5,6.
0.1
0.2
0.3
MICHIGAN mg/l N
(Y-X) on X
.04
.02
.00
-.02
-.04
LONDON-MICHIGAN mg/l N
0.1
0.2
0.3 mg/l N
Difference = 0.023 + 0.3% Michigan
correlation = 0.025
Sy.x = 0.015
off scale data excluded
MICHIGAN

FIGURE 3

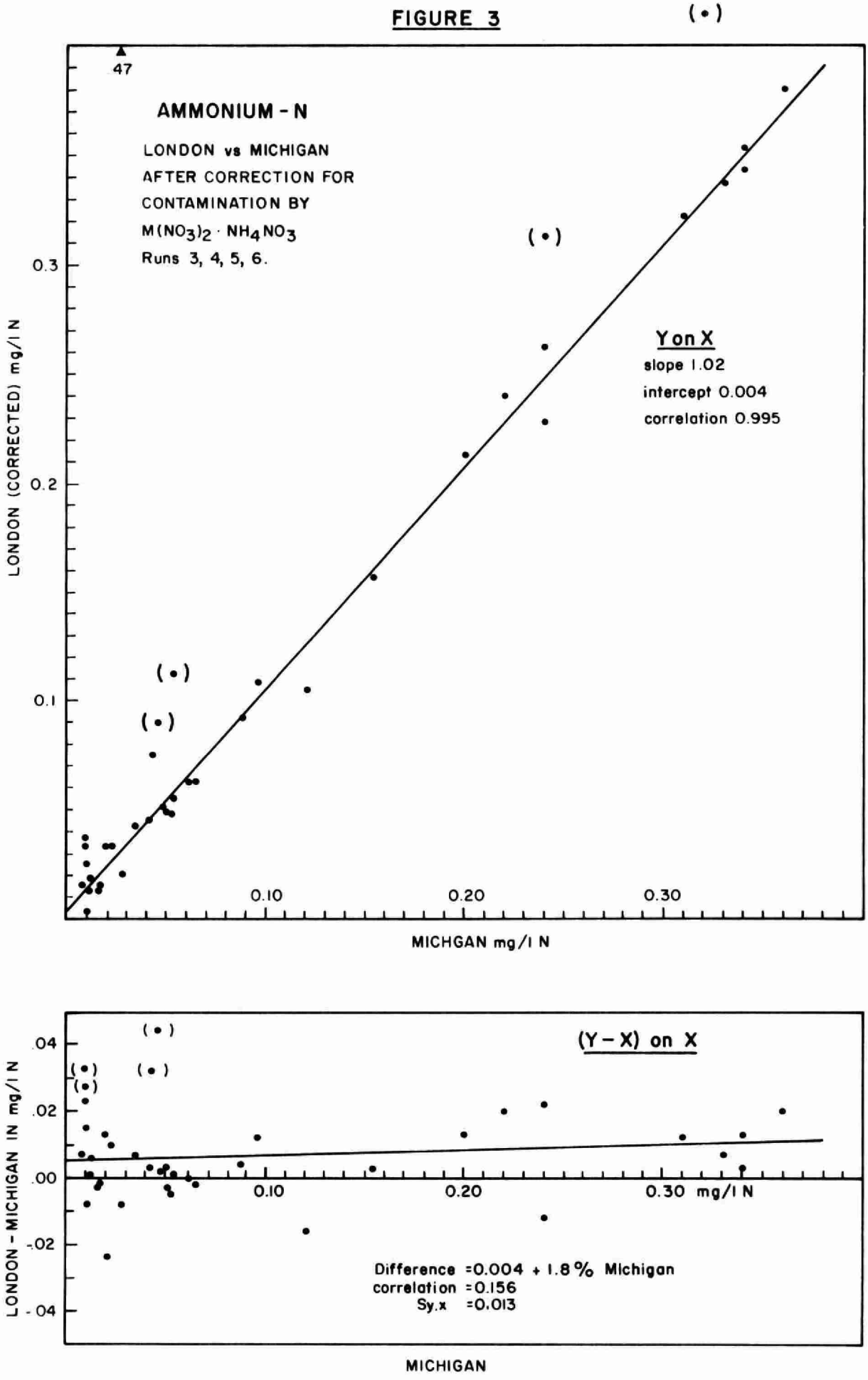

(•)
47
AMMONIUM - N
LONDON vs MICHIGAN
AFTER CORRECTION FOR
CONTAMINATION BY
$M(NO_3)_2 \cdot NH_4NO_3$
Runs 3, 4, 5, 6.
Y on X
slope 1.02
intercept 0.004
correlation 0.995
LONDON (CORRECTED) mg/l N
0.3
0.2
0.1
0.10
0.20
0.30
MICHGAN mg/l N
(Y - X) on X
LONDON - MICHIGAN IN mg/l N
.04
.02
.00
-.02
- .04
0.10
0.20
0.30 mg/l N
Difference =0.004 + 1.8% Michigan
correlation =0.156
Sy.x =0.013
MICHIGAN

FIGURE 4 Reactive Phosphates – London vs Michigan

to demonstrate changes in character and level of contamination from run to run.

Run 1, 2 : variable gross contamination
Run 3, 4, 5, 6 : except for a few points in run 3, background contamination of less than 0.003 mg/l (average)
Note: slope less than unity because Michigan reported unfiltered reactive phosphates

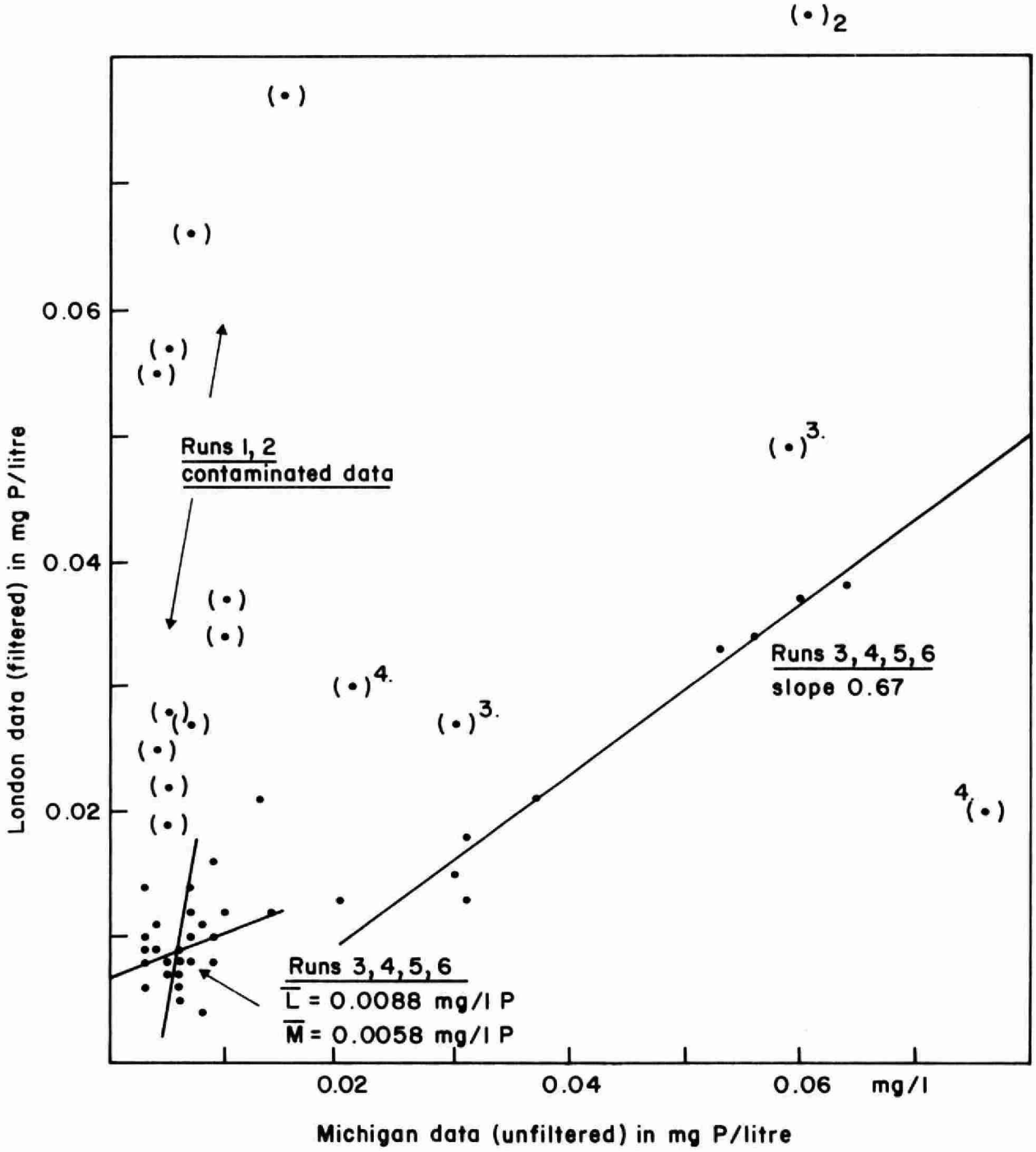


FIGURE 5 Reactive Phosphates – Toronto vs Michigan

to demonstrate changes in character and level of contamination from run to run.

Run 1: variable gross contamination
Run 2, 6 : constant low contamination
Run 3, 4, 5 : constant high contamination

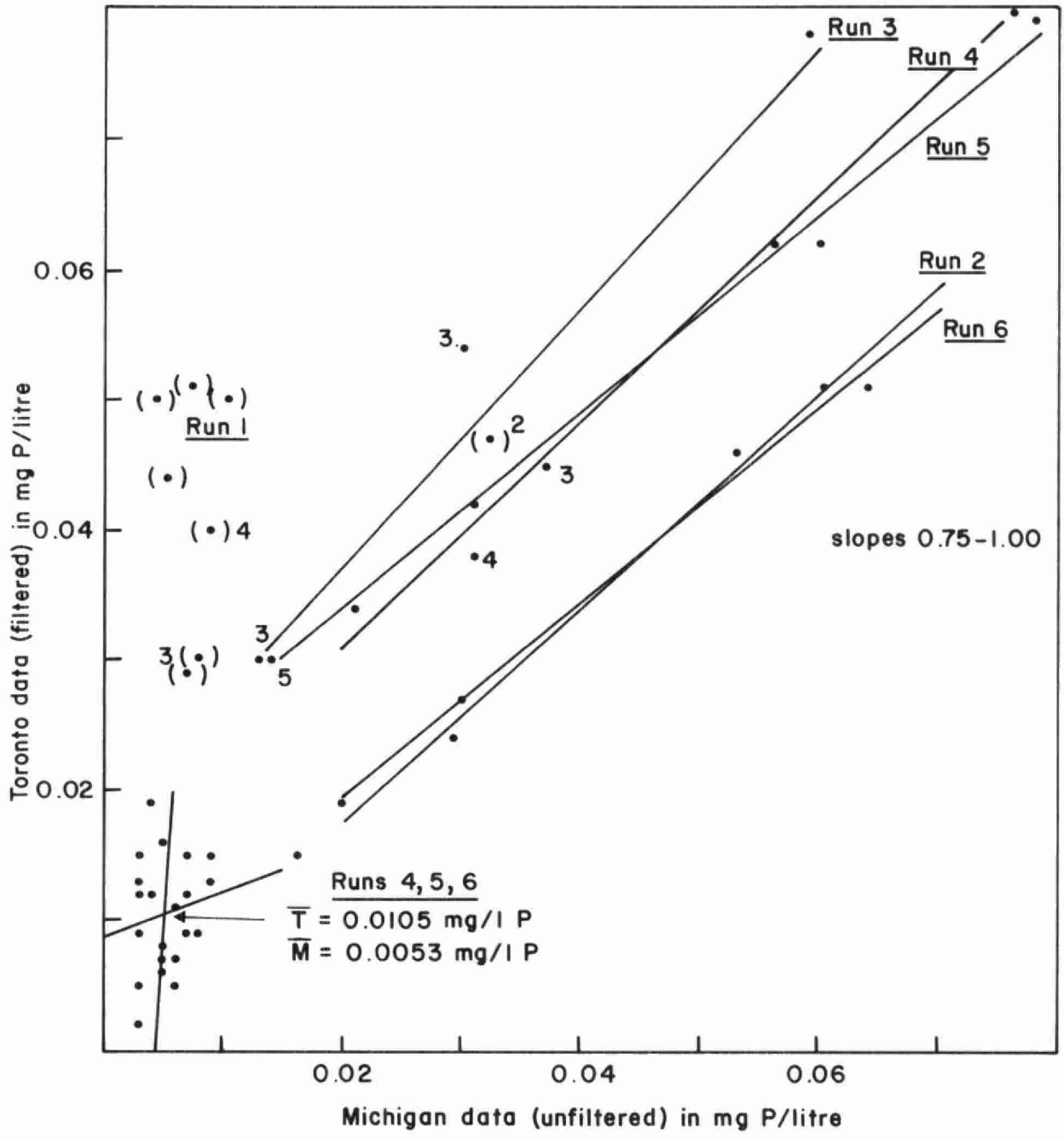
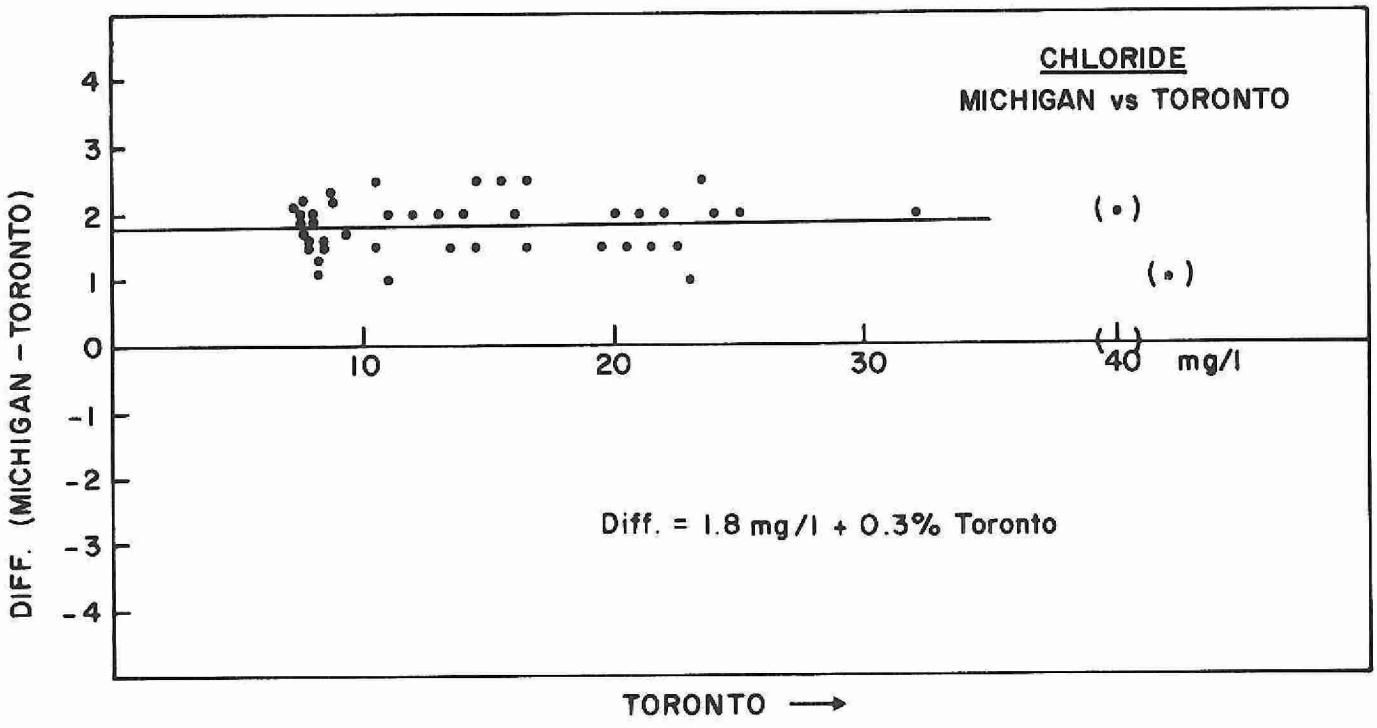
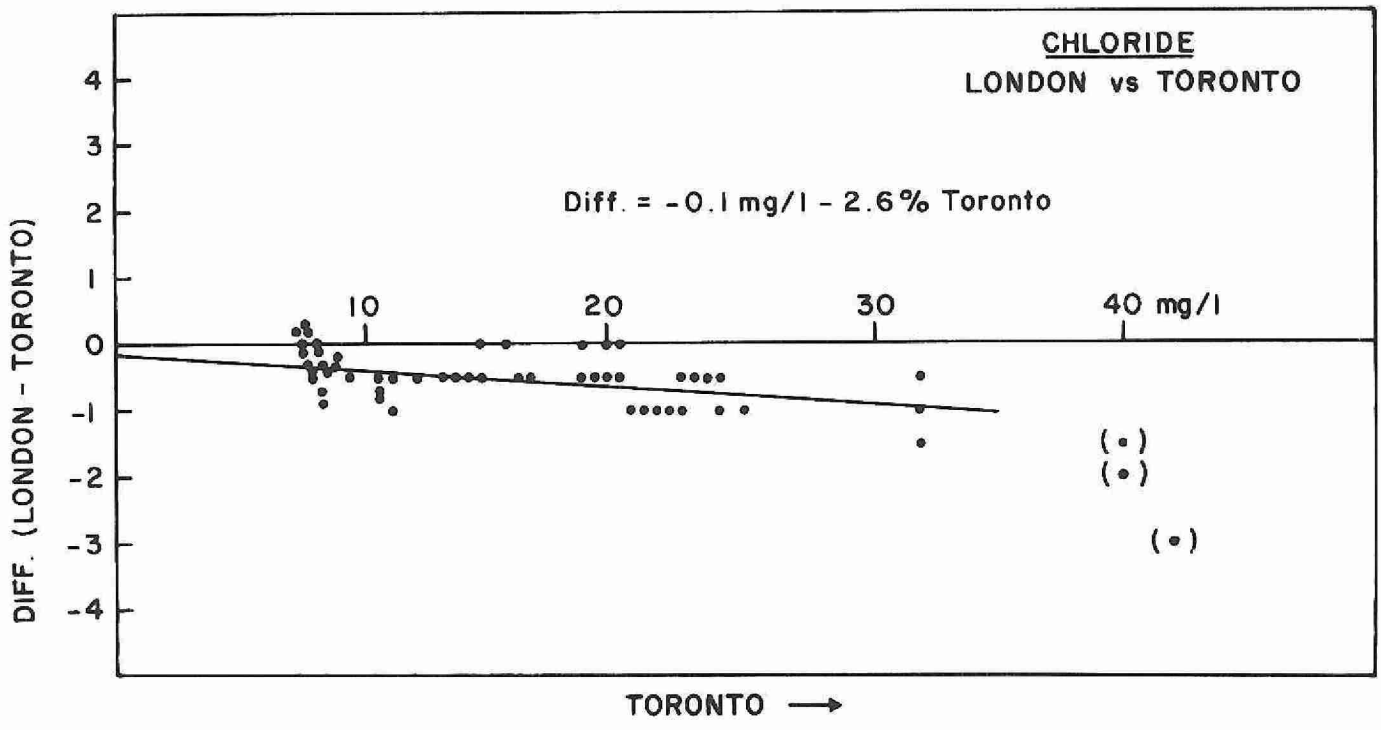


FIGURE 6 Chloride - to show nature and extent of bias between laboratories by plotting difference between labs vs concentration using Toronto as reference.





(15964)
MOE/INT/APFD
Ministry of the Environment
135 St. Clair Avenue West
Toronto, Ontario, Canada
M4V 1P5

	DATE DUE		

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King, Donald E.
Interagency
comparison between apfd
Ontario Michigan c.1 a aa